

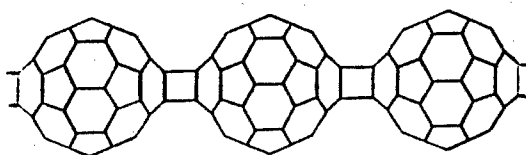
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**INTERNATIONAL
WINTERSCHOOL**

on

**ELECTRONIC PROPERTIES
of
NOVEL MATERIALS**



**FULLERENES
AND
FULLERENE NANOSTRUCTURES
HOTEL SONNALP**

**KIRCHBERG
TYROL
AUSTRIA**

**2.3 - 9.3.1996
PROGRAM**

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**INTERNATIONAL WINTERSCHOOL
ON
ELECTRONIC PROPERTIES
OF
NOVEL MATERIALS

FULLERENES AND
FULLERENE NANOSTRUCTURES**

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SCOPE

This winterschool will be organized in order to introduce advanced students and young researchers into the rapidly expanding field of fullerene research and applications. Particular attention will be paid to the nanostructured clusters, low dimensional compounds, polymers, endohedral compounds, new fullerene charge-transfer systems, new fullerene-derived molecules, and new fullerene composites as well as to open problems to traditional fullerenes. The progress in the understanding of the static and dynamical properties, the electronic structure, and the photonic response of these systems will be presented as analysed recently from structural, spectroscopic, transport and theoretical investigations.

NOTES FOR PARTICIPANTS

Time and location

The IWEP NM96 starts on Saturday, March 2, lunch time at the HOTEL SONNALP in Kirchberg / Tirol, Austria and extends to Saturday, March 9, breakfast. There will be a reception party on March 2, after dinner and a farewell party including dinner on March 8.

Transport

The hotel Sonnalp can be reached by private car from downtown Kirchberg by driving about one kilometer towards Aschau. Participants arriving at the railway station in Kirchberg or Kitzbühl should hire a taxi to get to the hotel.

Addresses

The address of the winterschool is:

IWEP NM96, Hotel Sonnalp, A-6365 Kirchberg/Tirol, Austria

Tel: ++43 05357 2741, Fax: ++43 05357 2741 200

However, all questions concerning the IWEP NM96 should be directed to:

Prof. H. Kuzmany, Institut für Festkörperphysik, Universität Wien

Strudlhofgasse 4 A-1090 Wien, Austria

Tel: Austria (1) 313 67 - 3206

Telex: 116222-physica

Fax: Austria (1) 310 38 88

Internet: kuzman@pap.univie.ac.at

Participation

Participation at the IWEP NM96 is possible for students and scientists working in the field covered by the scope of the meeting. However, because of the limited space the participation requires prearranged acceptance by the organizers.

Contributions

All oral contributions will be presented in the new seminar room of the Hotel Sonnalp. Participants are invited to contribute comments to research and tutorial lectures where 10 minutes for discussion are reserved at each lecture. Overhead projections and slide projection ($5 \times 5 \text{ cm}^2$) will be possible. Posters will be presented in the hall of the seminar room.

Proceedings

The contributions to the IWEP NM96 will be published in a special issue at World Scientific Publishing Co Ltd. The expected date of appearance of the proceedings is August 1996.

Manuscripts

Guidelines for the preparation of the manuscripts will be distributed in Kirchberg. The manuscripts should be mailed to:

Dr. Siegmur ROTH
Max-Planck-Institut für Festkörperforschung
Heisenberstraße 1
D-70569 Stuttgart 80, FRG

Manuscripts can only be published if they arrive before April 3, 1996. They will be reviewed within the two following weeks. Acceptance of a contribution for presentation at the winterschool does not automatically include acceptance for publication in the proceedings.

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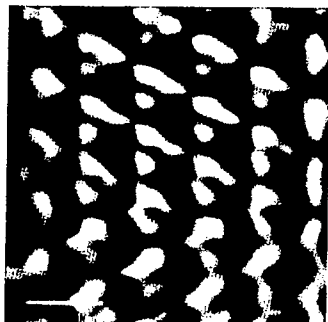
IWEPNM96 Program schedule: morning						
Sess. Day	08:30	09:00	09:30	Break	10:30	11:00
Sat 2.3.						11:30
Sun 3.3. FNST	Diff. by helical structures, from DNA to carbon nanotubes LUCAS B	Spectroscopy of carbon clusters CERMAK BRD	Determination by synchrotron x-ray diffraction of the endohedral nature for Y@C ₈₂ TAKATA J			El. prop. & struct. of metallofullerenes NAGASE J
Mon 4.3. AC60	Formation & morph. of polymer fibers PEKKER H	Magn. properties of the A _n C ₆₀ onductors FORRO CH	Structure of the full. dimer phase ... STEPHENS USA	O F F	NMR studies of the el. & mag. prop. of ... ALLOUL F	Thermodynamics of phase transform. in AC ₆₀ GRANASY H
Tue 5.3. CNTB	Carbon & CNT ZETTL USA	Novel catalysts on carbon nanotubes TSANG UK	CNT & graph. onions pyrolytic BxCyNz TERRONES/HSU UK	E E	Field emission and el. properties of CNT films HEER CH	ESR Properties of aligned CNT CHAUVEY F
Wed 6.3. APPL	Superhard & elast. carbon nitride films STAFSTRÖM SE	Superhard & ultrah. mat. from C ₆₀ fullerite BAGRAMOV RU		B R	Self-assembly of full. in solution. & solid MIHAILOVIC SLO	Interaction of full. with surfaces BALOOCH USA
Thu 7.3. AXC60	Mixed alkali-alkaline earth fullerenes FISCHER USA	ESR contr. to the study of normal state in alkali full. PETIT F	⁸⁷ Rb and ¹³ C NMR of Rb ₃ C ₆₀ ZIMMER BRD	E A K	Infl. of long range interactions in C ₆₀ compounds SAWATZKY NL	Study of K _n C ₆₀ compounds with x>6 RUDOLF B
Fri 8.3. POFU	Polymerized fullerene structures SCUSERIA USA	R. and NMR studies of pressure polymer. C ₆₀ SOLDATOV S	Structure, stab. & vibr. prop. of polym. C ₆₀ FRAUENHEIM BRD		Dimer and cluster formation in C ₆₀ BURGER A	Excitons in solid C ₆₀ EDER NL
Sat 9.3.	Departure					Frenkel and charge-transfer excitons MUCCINI I

IWEPM96 Program schedule: afternoon							Sess. Day
12:00	18:30	19:00	19:30	20:00	20:30		
					Reception Party		Sat 2.3.
M	17:00	Recent advances with fullerenes:	N subst. on C ₆₀ : monom., dim., ...	Heterofulls & their intercal. in the solid state		Sun 3.3.	HETF
I		WUDL	ANDREONI	PRASSIDES			
N		USA	CH	UK			
I		Structure of C ₆₀ monolayers	Inorganic fullerene-like structures & NT	C ₆₀ molecules with a metallic outer layer	Fullerene-like Si and Ge incl. compounds	Mon 4.3.	NFST
W	18:30	MAXWELL	TENNE	MARTIN	TANIGAKI		
	SE	ZERBETTO*	ISR	BRD	J		
O		Lattice dyn. of RbC ₆₀ a neutron scattering invest.	AF & Fransitions in TDAE-C ₆₀ sing. cryst.		Poster I	Tue 5.3.	C60-
R		RENKER	BLINC				
K		TOSATTI	SLO				
S		Org. chem. of full: tectons and heterofullerenes	Synth. & chiroopt. properties of fullerene derivatives	ESR spect. studies of the spin state & ei. transfer at endoh. full.	special poster	Wed 6.3.	CHEM
H		HIRSCH	PRATO	DUNSCH			
		BRD	I	BRD			
O		Spectrosc. probes of high fullerene isomers:	Prod. & charact. of macroscopic amounts of alkali-metallofull.		Poster II	Thu 7.3.	ENDO
P		KAPPES	TELLGMANN				
S		BRD	BRD				
		DINSE	BRD				
		F-sec. time res. two photon photoemiss. of C ₆₀	Summary		Farewell	Fri 8.3.	PHOT
		JACQUEMIN	RIETSCHER				
		BRD	BRD				
17:00	Excited state sp.: isolated molecules and thin films	VARDENY				Sat 9.3.	
	USA						

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Molekulare Auflösung von Tetramethylthioharnstoff mit ECSTM (4,25 nm x 4,25 nm),
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WORKSHOP / AUSSTELLUNGEN

Zu unserem **WORKSHOP** in Wien am 9. Mai 1996, den wir zusammen mit der Technischen Universität veranstalten, möchten wir Sie gerne einladen. Vortragende werden sein:

Professor Dr. M. Grasserbauer
 Professor Dr. L. Balk
 Professor Dr. A. Coleman
 Professor Dr. H. Fuchs
 Professor Dr. H. J. Güntherodt
 Professor Dr. U. Hartmann
 Professor Dr. H. Niehus

Bitte melden Sie sich über unser Büro in Darmstadt an.

Außerdem würden wir uns freuen, Sie während der

DPG-Frühjahrstagung in Regensburg
vom 26.-28. März 1996 und bei der

ANALYTICA in München
vom 23.-26. April 1996 in Halle 21, Stand D 19

begrüßen zu können.

Rufen Sie uns bitte an, wenn Sie an weiteren
Informationen interessiert sind.

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PROGRAM

AND

ABSTRACTS

Fullerene Nanostructures

- 8:30 – 9:30 A.A. LUCAS, Facultes Universitaires N.D. de la Paix, Namur, B
Diffraction by Helical Structures from DNA to Carbon Nanotubes
- 9:30 – 10:00 I. CERMAK, MPI Heidelberg, FRG
Optical Spectroscopy of Carbon Clusters and Particles
- 10:00 – 10:30 Coffee break
- 10:30 – 11:30 M. TAKATA, Nagoya University, J
Determination by Synchrotron X-ray Diffraction of the Endohedral Nature of the Metallofullerene Y@C₈₂
- 11:30 – 12:00 S. NAGASE, Tokyo Metropolitan University, J
The Electronic Properties and Structure of Endohedral Metallofullerenes
- 12:00 – 17:00 Mini Workshops
- 17:00 – 18:30 Dinner

Heterofullerenes

- 18:30 – 19:30 F. WUDL, University of California, Santa Barbara, USA
Recent Advances with Fullerenes: The Heterofullerenes
- 19:30 – 20:00 W. ANDREONI, IBM Research Division, Rüschlikon, CH
The Effect of Nitrogen Substitution on C₆₀: Monomer, Dimer et al.
- 20:00 – 20:30 K.PRASSIDES, Sussex University, GB
Heterofullerenes and their Intercalated Derivatives in the Solid State

DIFFRACTION BY HELICAL STRUCTURES FROM DNA TO CARBON NANOTUBES

A.A. LUCAS

In 1952, one year before the momentous discovery of the structure of DNA, Cochran, Crick and Vand (CCV) published a paper on the theory of X-Ray diffraction by a regular monoatomic helix. Although helical protein structures were then the immediate targets for application of the theory, the paper was to play a crucial role in the intellectual path taken by Watson and Crick towards the double helix.

In this seminar, we first perform laser optical simulation experiments intended to illustrate the most important features of the B-DNA structure as revealed by the famous X-Ray fiber diagrams obtained by Rosalind Franklin. Next the basic mathematical ingredients of the CCV theory are presented. We then show that the theory finds a particularly straightforward application in the diffraction of electrons or X-Rays by the recently discovered carbon nanotubes. By describing a straight monolayer nanotube as made of a finite, discrete set of monoatomic helices, a closed, analytical formula is derived for the kinematic diffraction amplitude of a complete achiral or chiral nanotube. On the basis of this result, computer simulations of diffraction by single-wall and multiple-wall nanotubes are presented. In particular, the hexagonal streaking spot patterns observed in Transmission Electron Diffraction are quantitatively explained.

The description of diffraction by coiled nanotubes synthesized at ISIS requires several extensions of the CCV theory which will be discussed. The formalism also provides a powerful method for the simulation of actual, multi-wall nanotubes with defects.

8:30
FNST
1

OPTICAL SPECTROSCOPY OF CARBON CLUSTERS AND PARTICLES

I. Čermák, G. Monninger, H. Stopka-Ebeler and W. Krätschmer

Max-Planck-Institut für Kernphysik, Postfach 103980, D-69029 Heidelberg, Germany

Because of their chemical and astrophysical relevance, carbon clusters (i.e. molecules), carbon particles, and recently also fullerenes have been the topic of intensive scientific research.

To study the optical spectra of carbon clusters (ranging up to about C_{20}), we applied the technique of matrix isolation in which the small molecules of carbon vapor are co-deposited with an excess of argon onto a cryogenic substrate. From such matrices, we took spectra ranging from the UV to the IR. The samples were prepared under clean vacuum conditions. By heating the samples, diffusion of the smallest clusters within the matrix takes place. It leads to cluster-cluster reactions, i.e. to formation of larger species, which is connected to changes of the absorption intensities in the measured spectra. To identify the produced molecules, we investigated predominantly the IR spectral range: We compared our spectra with the available gas-phase data, and with theoretical predictions. We also measured the spectra of ^{12}C - ^{13}C isotopomeric species, and searched for intensity correlations between different IR lines belonging to the same species.

We also applied the matrix isolation technique to investigate the optical spectra of small, submicron-sized carbon particles: The particles were produced and trapped in cryogenic matrices, and their UV spectra were taken. In addition, we collected similar particles in vacuum using a quadrupole trap. The first results of this new experiment are presented.

9:30
FNST
2

DETERMINATION BY SYNCHROTRON X-RAY DIFFRACTION OF THE ENDOHEDRAL NATURE OF THE METALLOFULLERENE $Y@C_{82}$

M. TAKATA, M. SAKATA, H. SHINOHARA & Y. SAITO*

Nagoya University, Nagoya 464-01, Japan., *Mie University, Tsu 514 Japan

The synthesis of fullerenes encapsulating various metal atoms within the carbon cage (endohedral metallofullerenes) has stimulated wide interest because of their unusual structural and electronic properties. Observations using STM, EXAFS, HRTEM and ESR have strongly suggested that the metal atoms are indeed inside the fullerene cage. Theoretical calculations also indicate that this is the case. But until now, no structural model has been derived experimentally to confirm the endohedral nature of the metallofullerenes. In the present study, the first conclusive evidence of endohedral nature of the Metallofullerene $Y@C_{82}$ has been obtained via a Synchrotron X-ray powder diffraction study using the Maximum Entropy Method(MEM).

The $Y@C_{82}$ fullerene was separated and isolated by the two-stage high performance liquid chromatography(HPLC) method. The purity of the $Y@C_{82}$ fullerene was more than 99.9%. An X-ray powder pattern of $Y@C_{82}$ was measured by using Imaging Plate at Photon Factory BL-6A2. The wavelength of incident X-rays is 1.0Å. The space group is assigned to $P2_1$, monoclinic. The experimental data were analyzed in an iterative way of combination of Rietveld analysis and the MEM. The reliable factor of the obtained MEM charge density is 1.4%. In the MEM charge density(Fig.1), there exist remarkably high densities just inside the C_{82} cage. The number of electrons around the maxima is about 38 which is very close to the atomic number of a yttrium atom. Evidently, the density maxima at the interior of the C_{82} cage is the yttrium atom. The present study revealed the fact that the yttrium atom is displaced from the centre of the C_{82} molecule and is strongly bound to the carbon cage.

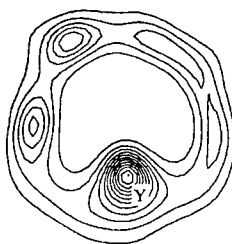


Fig.1 The section of the MEM charge density of $Y@C_{82}$.

The Electronic Properties and Structures of Endohedral Metallofullerenes

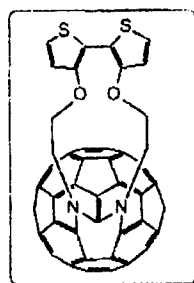
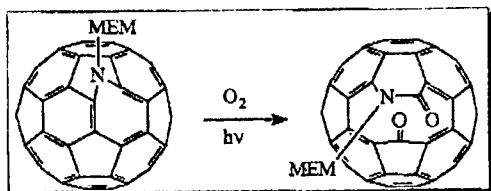
Shigeru Nagase

Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Hachioji, Tokyo 192-03, Japan

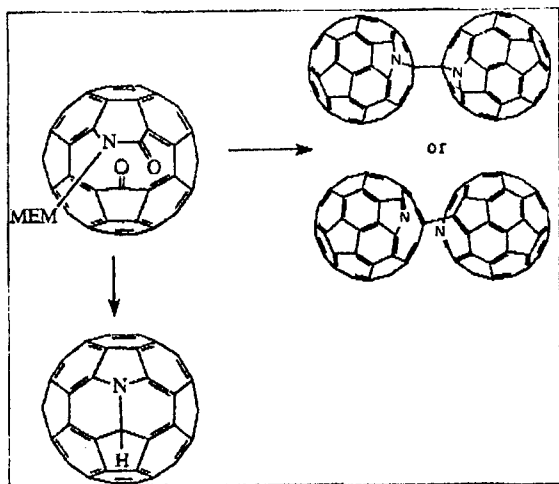
Encapsulation of a metal atom inside fullerene cages has attracted continuous interest because it could give rise to new molecules or materials which are not expected for empty fullerenes. Because of the difficulty in producing pure samples in large quantities, direct experimental characterization has been hindered. Recent important progress is marked by the successful isolation and purification of monometallofullerenes such as $Sc@C_{82}$, $Y@C_{82}$, $La@C_{82}$, and $Gd@C_{82}$. In addition, it has been demonstrated that two metal atoms can be trapped inside fullerene cages to form soluble and relatively air-stable dimetallofullerenes, and these successful isolation and purification have also been very recently achieved for $La_2@C_{80}$ and $Sc_2@C_{84}$. However, little is still known about the electronic properties and structures. Thus, we have undertaken the theoretical calculations. Our primary aim here is to disclose (a) how metals are trapped inside the fullerene cages, (b) what are the cage structures, (b) what are the electronic states of metals and cages.

RECENT ADVANCES WITH FULLERENES: THE HETEROFULLERENES. F. Wudl, Departments of Chemistry and Materials, University of California, Santa Barbara, CA 93106

Recent developments in the chemistry of buckminsterfullerene C_{60} will be presented. Investigations into azide addition for the synthesis of specific fullerene-containing molecules will be emphasized. Examples are shown below. A special emphasis will be given to the heterofullerene $C_{59}N$ derivatives such as the dimer and $C_{59}HN$.



18:30
HETF
1



The Effect of Nitrogen Substitution on C_{60} :
Monomer, Dimer et al.

19:30
HETF
2

Wanda Andreoni[†] and Alessandro Curioni^{1,2}

¹IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

²Scuola Normale Superiore, I-56014 Pisa, Italy

The synthesis of heterofullerenes where the C_{60} unit has one atom replaced by nitrogen, is a very recent success of Wudl's group in Santa Barbara.¹ We shall present brand new results of density-functional theory based calculations of equilibrium structures, vibrational spectra and electronic properties.

HETEROFULLERENES AND THEIR INTERCALATED DERIVATIVES IN THE SOLID STATE20:00 Kosmas Prassides

HETF

3 School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

The recently synthesised azafullerene solid has been studied by synchrotron X-ray diffraction both as a function of temperature and pressure. At ambient pressure, the as-prepared solid adopts a hexagonal crystal structure that persists in the temperature range between 80 and 500 K. Angle-dispersive X-ray diffraction data to pressures in excess of 20 GPa reveal a smooth evolution of the (c/a) ratio which reaches a plateau of 1.633 in the vicinity of 5 GPa. Supplementary information on the structure and morphology has been also obtained by SEM and TEM experiments. Sublimation of the azafullerene solid leads to a different low-symmetry structural form which shows clear evidence of superlattice formation consistent with the presence of dimeric (C₅₉N)₂ units. Reaction of the azafullerene solid with potassium and rubidium leads to the isolation of crystalline derivatives with stoichiometry K₆C₅₉N and Rb₆C₅₉N. Temperature- dependent synchrotron X-ray diffraction data reveal body-centred-cubic structures, essentially isostructural with the analogous derivatives of C₆₀ and comprising of monomeric (C₅₉N)₆- units.



CONCLUSIONS The authors would like to thank the National Science Foundation for the support of this work.

A₁C₆₀

- 8:30 – 9:00 S. PEKKER, Res. Inst. for Solid State Physics, Budapest, H
Formation and Morphology of (KC₆₀)_n Polymer Fibres
- 9:00 – 9:30 L. FORRO, EPF Lausanne, CH
Pressure and Disorder Effect on Magnetic Properties of the A₁C₆₀ Conductors
- 9:30 – 10:00 P. STEPHENS, SUNY Stony Brook, USA
Structure of the Fullerene Dimer Phases KC₆₀ and RbC₆₀
- 10:00 – 10:30 Coffee break
- 10:30 – 11:00 H. ALLOUL, Universite Paris-Sud, Orsay, F
NMR Studies of the Electronic and Magnetic Properties of AC₆₀ (A=K,Rb,Cs)
- 11:00 – 11:30 F. RACHDI, Universite Montpellier, F
High Resolution NMR Investigation of One and Two Dimensional Polymerized C₆₀
- 11:30 – 12:00 L. GRANASY, Res. Inst. for Solid State Physics, Budapest, H
Thermodynamics of Phase Transformations in AC₆₀ (A=K,Rb,Cs) Alkali Fullerides
- 12:00 – 17:00 Mini Workshops
- 17:00 – 18:30 Dinner

New Fullerenic Structures

- 18:30 – 19:00 A.J. MAXWELL, Uppsala University, S
Electronic and Physical Structure of C₆₀ Monolayers on Al(111) and Al(110)
- 19:00 – 19:30 F. ZERBETTO, Universita d.S. Di Bologna, I
Penalty Functions and Propensity Rules for the Stability of Fullerenes
- 19:30 – 20:00 R. TENNE, Weizmann Institute, Israel
Inorganic Fullerene-like Structures and Nanotubes of MX₂ (M=W,Mo;X=S,Se)
- 20:00 – 20:30 T.P. MARTIN, MPI Stuttgart, FRG
C₆₀ Molecules with a Metallic Outer Layer
- 20:30 – 21:00 K.TANIGAKI, NEC Corporation, Tsukuba, J
Fullerene-like Si and Ge Inclusion Compounds

FORMATION AND MORPHOLOGY OF $(\text{KC}_{60})_n$ POLYMER FIBERS

S. Pekker¹, M. Carrard², L. Forro² and L. Mihaly³

¹Research Institute for Solid State Physics, H-1525 Budapest, POB 49, Hungary

²IGA, Ecole Polytechnique Federale de Lausanne, 1015 Lausanne, Switzerland

³Department of Physics, SUNY at Stony Brook, Stony Brook, NY 11794-3800

The coevaporation of alkali metals ($A=\text{K, Rb}$) and C_{60} with 1 to 1 stoichiometry has been studied. $A_1\text{C}_{60}$
 Either microcrystalline single phase AC_{60} polymers or multiphase materials containing a few
 hundred micron crystallites were formed depending on the experimental conditions. The large
 mosaic crystals were disintegrated to bundles of polymeric AC_{60} fibers upon a treatment in
 toluene while their C_{60} content was dissolved. The structure and morphology of KC_{60} fibers have
 been investigated by optical microscopy, IR spectroscopy and electron microscopy. The detailed
 analysis of electron diffraction patterns and micrographs reveals that the fibers are in fact
 accordion shaped ribbons consisting of twins of single crystalline lamellae. The direction of
 polymerization does not coincide with the long axis of the fibers.

8:30

 $A_1\text{C}_{60}$

1

PRESSURE AND DISORDER EFFECT ON MAGNETIC PROPERTIES OF THE $A_1\text{C}_{60}$ CONDUCTORS

L. Forro

Physics Department, Ecole Polytechnique Federale de Lausanne, 1015 Lausanne,
 Switzerland

9:00

 $A_1\text{C}_{60}$

2

The 1D polymeric structure of the orthorhombic phase of the $A_1\text{C}_{60}$ conductors
 suggested 1D electronic structure, with a spin density wave instability at low
 temperatures in Rb_1C_{60} and Cs_1C_{60} . Theoretical calculations give rather a 3D
 electronic structure for these compounds. We will address this issue by studying the
 effect of pressure and disorder on the spin relaxation by ESR which is distinctly
 different for 1D and 3D conductors:

This work is performed with: G. Baumgartner, A. Sienkiewicz, O. Chauvet, F. Beuneu
 and H. Alloul.

STRUCTURE OF THE FULLERENE DIMER PHASES KC60 AND RbC60

Peter W. Stephens and Goetz Bendele, SUNY Stony Brook,
Gabor Oszlanyi, Gabor Bortel, Gyula Faigel, and Laszlo Granasy, Research
Institute for Solid State Physics, Budapest, Hungary,
Laszlo Forro, Ecole Polytechnique Federal de Lausanne, Switzerland

Previously published work showed that the insulating quenched phase is made up of C60 dimers, but it was not possible until now to resolve the fullerene orientation and therefore the bonding geometry. With improvements in sample preparation technique, we are finally able to obtain clean, single-phase x-ray diffraction spectra of the dimer phase in both of the title compounds. We find that the agreement between measured and calculated diffraction spectra is quite sensitive to the fullerene orientation, and have obtained definitive results on the correct structure. The dimer molecule is bonded through a single carbon atom on each fullerene, and not the 2+2 cycloaddition of the room temperature polymer phase. This confirms our earlier thermodynamic evidence that the dimer phase is not structurally related to the polymer.

NMR STUDIES OF THE ELECTRONIC AND MAGNETIC PROPERTIES OF AC60 (A=K, Rb, Cs).

H. Alloul^{1,2}, V. Brouet¹, Y. Yoshinari¹, E. Lafontaine³, L. Malier⁴ and L. Forro⁵

¹ Physique des Solides, UA2 CNRS, Université Paris-Sud, 91405 Orsay, (France)

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⁵ Laboratoire de Physique des Solides Semicristallins, IGA, EPFL 1015, Lausanne, (Switzerland).

Previous experiments have shown that in the orthorhombic phase of AC60 compounds the distance between C60 balls is unusually small in one direction. A polymeric linear chain structure has therefore been proposed from detailed crystallographic data. We have shown at Kirchberg last year that Magic Angle Spinning (MAS) measurements allow to greatly resolve the unusually broad ¹³C NMR spectra of the polymer phase of RbC60 and to confirm the existence of an ordered state. More detailed data and Very High Speed MAS allow us to perform accurate intensity analyses of the various components of the spectra. The signal of the bonding sites has been resolved, and displays all the features expected for sp³ bonding between the C60 molecules.

Both low T wide band measurements and MAS techniques have been extensively used to compare the electronic structures of the Rb, Cs and K polymer phases. Comparison of the spin lattice relaxation (T₁) data on the ¹³C and alkali NMR, establishes the importance of 1D magnetic correlations in RbC60 and CsC60, while KC60 displays a classical 3D behaviour. Measurements at low T reveal the existence of a magnetic transition at about 25K in the Rb and Cs polymers. The data supports the occurrence of a spin flop AF phase with relatively large local moments (m=0.5mB). MAS measurements allow to compare the distribution of spin densities on the carbon sites in the three polymer systems and to discuss the incidence of the electronic structure on the dimensionality of their magnetic properties.

High Resolution NMR Investigation of One and Two Dimensional Polymerized C60

F. Rachdi, C. Goze

Groupe de Dynamique des Phases Condensées, UMR 233

Université Montpellier II, 34095 Montpellier, France

M. Nunez-Regueiro, Centre de Recherche sur les Très Basses Températures

CNRS, BP 166 Cedex 09, 38042 Grenoble, France

K.F. Thier, G. Zimmer, M. Mehring, 2-Physikalisches Institut, Universität Stuttgart
Pfaffenwaldring 57, Stuttgart, Germany

11:00
A₁C₆₀
5

We report on high resolution ¹³C NMR measurements on Orthorhombic 1D and Rhombohedral 2D polymerized C₆₀ under high pressure. By spinning the samples up to 12KHz, we were able to identify two isotropic resonances at 146 ppm and 73.5 ppm for both polymers. Furthermore, the line around 146 ppm in the 2D spectrum is splitted into five components at 149.1 ppm, 147.9 ppm, 145.2 ppm 139.6 ppm, 134.8 ppm. The static orientational disorder of the pristine fcc C₆₀ provided by the pressure must be at the origin of the observed inequivalent carbons in both systems. The ¹³C NMR lineshape simulation of the obtained spectra are compatible with the suggested polymeric structures where the C₆₀ molecules are connected by [2+2] cycloadditions. We also present NMR data on polymeric phase A₁C₆₀ with A=Rb and Cs. Static and high resolution ¹³C spectra show a close analogy between the polymer phase Rb₁C₆₀ and Cs₁C₆₀. From temperature dependent lineshift we have extracted information about the hyperfine couplings and electron density distribution on the C₆₀ molecules. The data also support the existence of the sp³ like bonding type between the molecules.

THERMODYNAMICS OF PHASE TRANSFORMATIONS IN A₁C₆₀ (A=K, Rb, Cs) ALKALI FULLERIDES

L. Gránásy, S. Pekker, M. Tegze

Research Institute for Solid State Physics, H-1525 Budapest, POB 49, Hungary

L. Forró

Departamente de Physique, Ecole Polytechnique Federale de Lausanne, 1015-Lausanne, Switzerland

11:30
A₁C₆₀
6

The phase transformations between stable and metastable modifications of A₁C₆₀ (A=K, Rb, Cs) alkali fullerenes were studied by differential scanning calorimetry. The relative Gibbs free energies of the fcc, dimer, polymer, phase separated, etc. structures are evaluated from the measured transformation temperatures and enthalpies. The relative stability of the polymer and phase separated states of K₁C₆₀ has been studied in detail. Contrary to recent indications [1,2], the polymer phase does not show phase separation at low temperatures. This accords with the finding that below appr. 360 K the polymer has a lower Gibbs free energy than the phase separated "intermediate" state of K₁C₆₀ [3]. Thus in all three systems the polymer is the low temperature stable form.

- [1] D.M. Poirier, J. H. Weaver, Phys. Rev. B 47, 10959 (1993).
- [2] J. Robert, P. Petit, J. E. Fischer, Synth. Met., in print.
- [3] L. Gránásy, S. Pekker, L. Forró, Phys. Rev. B, in print.

Electronic and physical structure of C60 monolayers on Al(111) and Al(110)

A. J. Maxwell, P. A. Brühwiler, S. Andersson, D. Arvanitis, B. Hernnäs, O. Karis, D. C. Mancini and N. Mårtensson. Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden.

S. M. Gray, M. K.-J. Johansson, and L. S. O. Johansson. Department of Synchrotron Radiation Research, Lund University, Sölvegatan 14, S-223 62 Lund, Sweden.

We have studied C60 monolayers on the (111) and (110) Al surfaces using LEED, STM, Photoelectron Spectroscopy (PES) and C 1s X-ray Absorption (XAS), as well as C 1s autoionization. A C60 monolayer on Al(111) forms a metastable $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ phase if deposited at room temperature, which reconstructs to a stable (6×6) phase at temperatures normally used to anneal the Al crystal. The details of the structure were studied using STM, as well as core level PES studies of the Al 2p level. STM indicates that two thirds of the molecules remain in a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ configuration, whereas the remaining one third are raised approximately 1.9 Å above the surface. Al 2p PES indicates that Al atoms have most likely followed this reconstruction-about one sixth are displaced from their original positions to a location of lower charge density. Valence PES and XAS show a relatively large broadening of all valence and conduction levels, but no sign of charge transfer, which indicates that any such transfer is small and/or distributed over several eV near Ef. We interpret these facts as strong evidence for predominantly covalent bonding of the fullerenes to the surface, which is consistent with previous studies of the interaction of Al with other aromatic molecules. PES, XAS and LEED results for the Al (110) surface show that the strength of the substrate adsorbate bonding interaction is highly dependent on the surface structure.

Penalty functions and propensity rules for the stability of fullerenes

Francesco Zerbetto

Dipartimento di Chimica "G. Ciamician", Università degli Studi Di Bologna, V. F.

Selmi 2, 4126 Bologna, Italy

Recent computational results on systematic calculations of complete sets of fullerenes - which may comprise up to several thousands of possible isomers - are presented in terms of penalty functions for the formation of pentagon-pentagon adjacencies, square, and heptagons. The effect of charging on the stability of IPR fullerenes is also explored. Non-classic odd-numbered fullerenes are generated via three routes. A few of propensity rules are devised to narrow down the number of isomers one must consider to establish their connectivity.

INORGANIC FULLERENE-LIKE STRUCTURES AND NANOTUBES OF
MX₂ (M=W,Mo;X=S,Se), R. Tenne, Y. Feldman, M. Homyonfer, and G.L. Frey,
Department of Materials and Interfaces, Weizmann Institute, Rehovot 76100,
Israel

Extensive investigation of the newly discovered inorganic fullerene-like (IF-MX₂) and nanotubes of metal dichalcogenides, is reported. Our findings suggest that the IF-MX₂ material constitute a new phase between the low temperature amorphous precursor and the bulk 2H polymorph, which is obtained upon annealing above 950°C. The energy bandgap of the NP, was found to be somewhat smaller than that of the bulk 2H phase, and possible explanations for that phenomenon are forwarded. New synthetic routes allow for the production of a few grams of IF-WS₂ (macrosynthesis), on the one hand, and a single IF in a predetermined position (nanosynthesis), on the other hand. Synthesis of new IF-MX₂ from different layered compounds, will be reported. Measurements of the optical properties, will be reported.

19:30
NFST
3

C₆₀ Molecules with a Metallic Outer Layer

T.P. Martin
Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1, 70569 Stuttgart, FRG

20:00
NFST
4

The properties of metal coated fullerene molecules, C₆₀M_x, can be studied in the gas phase using the techniques of mass spectrometry. Alkaline earth metals can be deposited on C₆₀ layer by layer. Each time a new icosahedral layer is complete, the cluster is particularly stable. The properties of alkali metal coated C₆₀ on the other hand are determined not by the geometric structure, but by the electronic structure. The electrons are organized in shells causing the clusters to behave like giant atoms. However, the optical response of such clusters is dominated by collective excitations best described as plasmons.

FULLERENE-LIKE Si AND Ge INCLUSION COMPOUNDS

Katsumi Tanigaki, Otto Zhou, Sadanori Kuroshima

Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka,
Tsukuba 305, Japan

Carbon fullerenes have attracted considerable attention in the scientific community because of their intriguing molecular structures and the potential of leading to materials with interesting properties. Similar structures are also observed in other group IV elements. For example, closed cage structures of Si and Ge can be formed when alkali metal silicides and germanides are distilled under controlled conditions. These compounds, often with the clathrate hydrate structure, are composed of Si or Ge fullerenes with the cluster sizes as small as 20 (with twelve pentagons). Metal atoms can also be trapped inside the fullerene cages, forming inclusion/endohedral solids. In contrast to the carbon fullerenes, the fullerene cages in Si and Ge clathrates are inter-connected by the covalent sp^3 bonds. Si and Ge clathrate compounds are interesting materials as they are expected to have band gaps similar to that of the porous silicon. Superconductivity was recently reported in ternary silicon clathrate $Na_xBa_6Si_{46}$, where the metal atoms are encapsulated by the Si_{20} and Si_{24} cages which crystallize into a structure reminiscent of the $A15 Ba_3C_{60}$.

We have synthesized new Si and Ge inclusion compounds by the solid state reaction method that has led to the formation of $Na_2Ba_6Si_{46}$. The formation, structure and chemical composition of these materials have been studied by DSC, x-ray diffraction and electron microscopy techniques. Their basic properties have been characterized by DC magnetization and XPS measurements. In this talk we will present some preliminary results from our studies of the Si and Ge inclusion compounds and contrast their structures and properties to those of the carbon fullerenes.

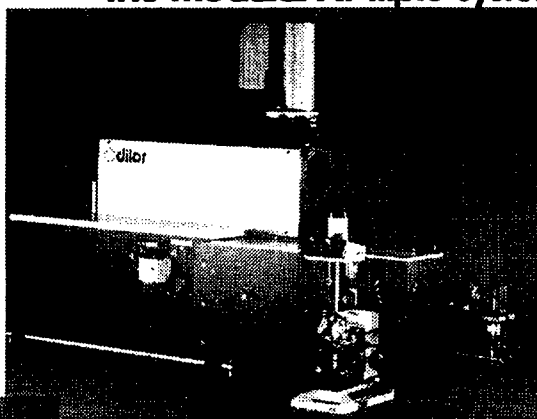
Raman at work: Systems for the Raman spectroscopy made by DILOR

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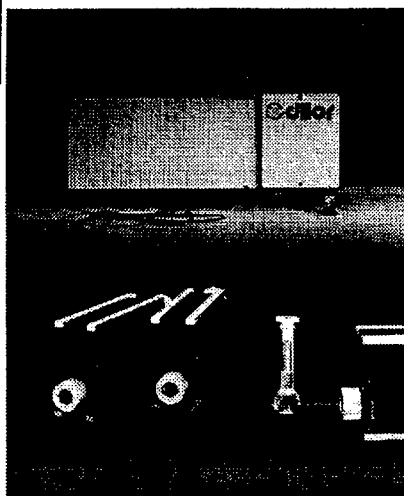
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Carbon Nanotubes

- 8:30 – 9:00 A. ZETTL, University of California, Berkeley, USA
Carbon and Non-carbon Nanotubes
- 9:00 – 9:30 S.C.E. TSANG, University of Reading, Whiteknights, UK
Preparation of Novel Catalysts on Carbon Nanotubes
- 9:30 – 10:00 M.TERRONES and W.K. HSU, University of Sussex, Brighton, UK
Morphology Effects of Catalytic Particles in Pyrolytic Grown $B_2C_2N_2$ Nanofibers and Nanotubes
- 10:00 – 10:30 Coffee break
- 10:30 – 11:00 W. A. de HEER, EPFL, Lausanne, CH
Field Emission and Electronic Properties of Carbon Nanotubes Films
- 11:00 – 11:30 L. DEGIORGI, ETH-Zürich, Zürich, CH
The Optical Response of Carbon Nanotubes
- 11:30 – 12:00 O. CHAUVET, Institut des Matériaux de Nantes, F
ESR Properties of Carbon Nanotubes
- 12:00 – 17:00 Mini Workshops
- 17:00 – 18:30 Dinner

 AC_{60} and C_{60}^-

- 18:30 – 19:00 B. RENKER, Forschungszentrum Karlsruhe, Karlsruhe, BRD
Lattice Dynamics of RbC_{60} in its Rotator, Polymer and Dimer Phase: A Neutron Scattering Investigation
- 19:00 – 19:30 E. TOSATTI, SISSA/INFN/ICTP, Trieste, I
Suprises in the Orbital Magnetic Moment and g-Factor of the Dynamic Jahn-Teller Ion C_{60}^-
- 19:30 – 20:00 R.BLINC, J. Stefan Institute, Ljubljana, SLO
Antiferromagnetic and Ferromagnetic Transition in Pure and Doped TAED- C_{60} Single Crystals

Poster session I: fullerene nanotubes, chemistry, fullerenes

Carbon and Non-carbon Nanotubes

Alex Zettl

Department of Physics, University of California at Berkeley, and
Materials Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley, CA 94720

Carbon and non-carbon nanotubes are predicted to have interesting and unique electrical and mechanical properties. I will discuss some of the theoretical predictions and relevant experiments on BxCyNz nanotube structures, including mechanical deformations, field emission, and on-tube nanoscale devices.

8:30
CNTB
1

Preparation of Novel Catalysts based on Carbon Nanotubes

S.C.E. Tsang^a, Y.K. Chen^b and M.L.H. Green^b

^a The Catalysis Research Centre, Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK

^b The Catalysis Centre, Inorganic Chemistry laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK

Abstract

The discovery of carbon nanotubes by Iijima¹ and the reported method of their large scale production by Ebbesen and Ajayan² have stimulated a great deal of research interest on this new form of carbon. It has been suggested that this carbon material may find applications in catalysis, separation and storage technology and in the development of materials with new magnetic and electronic properties and these might be modified by introducing foreign materials into the nanotubes. We have recently reported a simple yet efficient method for the selective opening of carbon nanotubes using nitric acid³. Refluxing the carbon nanotubes in nitric acid allows selective attack of the more reactive tube ends (oxidation) resulting in the opening of the tubes in very high yields (>80%). Once opened the tubes could be filled by the simple stirring with solutions of a wide variety of materials. The ability to fill these carbon nanotubes with chemicals, particularly of materials with catalytic interest suggest that many exciting possibilities for further developments in catalysis. Here we describe the preparation, characterisation and testing of *nanosized* metal oxides, mixed metal oxides and metals inside the carbon nanotubes as novel catalysts. We found that some metal oxides and metal nanocrystals have a preferred orientation of the crystal planes with respect to tube axis, suggesting the possibility of controlling highly dispersed particles with specific exposed crystallographic faces for a particular catalysis reaction. We also report the immobilisation of enzymes (biocatalysts) inside the carbon nanotubes. We demonstrate the use of carbon nanotube as a benign host and its ability to encapsulate enzyme molecules within a protected environment.

9:00
CNTB
2

PRODUCTION OF CARBON NANOTUBES AND GRAPHITIC ONIONS BY CONDENSED PHASE ELECTROLYSIS

W. K. Hsu, M. Terrones, J. P. Hare, D. R. M. Walton and H. W. Kroto

School of Chemistry and Molecular Sciences

University of Sussex

Falmer, Brighton, BN1 9QJ, U.K.

Graphitic nanomaterials including carbon nanotubes, onion-like and encapsulated nanoparticles have been produced by electrolysis using graphite electrodes immersed in molten LiCl at 600°C under different environments (Argon, vacuum and air). After applying a DC current (ca. 10-20 Amps.), an etched surface on the graphite cathode was observed and various types of graphitic nanostructures (e.g. encapsulated LiC particles, carbon nanotubes and graphitic onions) are formed during this process. Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM) reveal that up to 60 % of the carbon which is released from the cathode may have nanotube structures. X-ray and electron diffraction analyses show the presence of encapsulated LiC in some of the nanoparticles and nanotubes, this may be useful as nano-scale batteries in electronics. Li₂O deposits are also observed surrounding the particles and tubes when the electrolysis is carried out in air. A possible growth mechanism and new routes in the nanotube production are discussed.

MORPHOLOGY EFFECTS OF CATALYTIC PARTICLES IN PYROLYTIC GROWN B₂C₃N₂ NANOFIBRES AND NANOTUBES

M. Terrones^a, A. M. Benito^a, C. Manteca-Diego^b, W. K. Hsu^a, O. I. Osman^a, J. P. Hare^a, D. G. Reid^a, H. Terrones^a, K. Prassides^a, D. R. M. Walton^a and H. W. Kroto^a

^a School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, U.K.

^b Departamento de Tecnologías Especiales aplicadas a la Aeronáutica
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^c Instituto de Física, UNAM, Apartado Postal 20-364, México, D. F. 01000, México

Pyrolysis of CH₃CN·BCl₃ at ca. 900°C - 1000°C over Co powder generates novel B₂C₃N₂ nanofibres and nanotubes possessing various morphologies (e.g. curled, branched and bent). In these experiments the metal particle plays an important role in the nanotube growth since the accretion of carbon atoms appears to occur on the metal surface. It is also likely that the growth velocities depend on the exposed area of the particle resulting in differences in wall growth rates which appears to be responsible for the curvature of the structures. High Resolution Transmission Electron Microscopy (HRTEM) observations and Electron Energy Loss Spectroscopy (EELS) studies suggest that the graphitic filaments produced consist of ca. [BC₂N]_z, (z = 0.5-1), in which additional carbon is deposited on the tips where the metal particle is found. A possible growth mechanism is suggested and new synthetic/pyrolytic routes for the production of novel nanofibres and nanotubes containing boron, nitrogen and carbon are also discussed.

Field emission and electronic properties of carbon nanotubes films

Walter A. de Heer

EPFL, Lausanne, Switzerland

Carbon nanotubes are abundantly produced in carbon arc deposits, from which they can be extracted, purified and deposited to make aligned nanotube films. Carbon nanotubes are important since they are chemically and thermally stable nanoscopic objects that are easily produced and manipulated. Several carbon nanotube and nanotube film properties have recently been measured for example magnetic susceptibilities, dielectric functions and transport properties. Furthermore we recently found that the aligned nanotube films are also excellent electron emitters due to the sharp nanotube tips. Hence these films are good candidates for electron sources for flat panel CRT displays. The current status of nanotube electron injection into polymer films will also be discussed.

THE OPTICAL RESPONSE OF CARBON NANOTUBES

F. Bommeli¹, L. Degiorgi¹, L. Forro², W. Bacsa³ and P. Wachter¹

¹Laboratorium für Festkörperphysik, ETH-Zürich, CH-8093 Zürich

²Institut de Génie Atomique, Département de Physique, EPF-Lausanne, CH-1015 Lausanne

³Institut de Physique Expérimentale, EPF-Lausanne, CH-1015 Lausanne

11:00
CNTB
5

Band structure calculations have predicted metallic behaviour for the carbon nanotubes. In order to study the electrodynamic response with respect to this metallic state, we performed reflectivity measurements, made from the far-infrared up to the ultra-violet (i.e., from 1 meV up to 4 eV). We extracted the optical conductivity from the Kramers-Kronig transformation of the reflectivity spectra and analysed our data in terms of the effective medium model given by Maxwell-Garnett, where small conducting particles are dispersed in a dielectric medium. Within this model, a shift of the metallic Drude component from zero to higher frequency is predicted. Our experimental findings can be described by this phenomenological approach, suggesting an anisotropic metallic behaviour of the nanotubes.

ESR Properties of Aligned Carbon Nanotubes

O. Chauvet^{1,2}, G. Baumgartner², M. Carrard², W. Bacsa³,
W.A. de Heer³ and L. Forro²

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² Lab. Phys. des Solides semi-cristallins, IGA/DP, Ecole Polytechnique
Fédérale de Lausanne, CH-1015 Lausanne

³ Institut de Physique Expérimentale, D.P., Ecole Polytechnique Fédérale
de Lausanne, CH-1015 Lausanne

11:30
CNTB
6

Angle dependent conduction electron spin resonance of bulk, aligned and partially purified carbon nanotubes reflects the anisotropic character of the tubes. The low value of the Pauli susceptibility is consistent with a semimetal, the temperature dependence of the g factors as well.

Efficient charge transfer upon moderate doping with potassium is testified by the enhancement of the Pauli susceptibility and the washing out of the g factor anisotropy. Both pristine and K-doped nanotubes are good conductors as shown by their linewidth temperature dependence.

LATTICE DYNAMICS OF RbC₆₀ IN ITS ROTATOR, POLYMER AND DIMER PHASE: A NEUTRON SCATTERING INVESTIGATION

B. Renker, H. Schober*, F. Gompf, and R. Heid;
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 Postfach 3640, D-76021 Karlsruhe, Germany*
 *Institut Laue-Langevin, BP 156, F-38042 Grenoble, Cedex 9, France

Investigations of RbC₆₀ give evidence for characteristic differences in spectra of low-energy lattice vibrations between the high-temperature dynamically disordered and the low-temperature ordered polymer and dimer phases. These changes are consistent with the formation of inter-C₆₀ covalent bonds. Significant splittings of intramolecular modes occur in the polymer but not in the dimer phase, signaling remarkable differences in the intermolecular bondings. We can explain the main spectral features for all three modifications by a lattice dynamical model which includes translational and librational modes and covers the frequency region of external and internal molecular vibrations. A softening of lattice modes is observed as a precursor of the 390 K order / disorder transition. Evidence is obtained for an anomalous low-temperature behaviour of low-energy modes in the polymer phase, but a connection with the proposed metal-to-insulator transition at 50 K cannot be established.

SURPRISES IN THE ORBITAL MAGNETIC MOMENT AND g-FACTOR OF THE DYNAMIC JAHN-TELLER ION C₆₀⁻

Erio Tosatti^{1,2,3*}, Nicola Manini^{1,2,4**}, and Olle Gunnarsson^{5***}

¹ SISSA, Trieste, ² INFM, ³ ICTP, Trieste, ⁴ ESRF, Grenoble,

⁵ MPI für Festkörperforschung, Stuttgart.

We have calculated the magnetic susceptibility and g-factor of the isolated C₆₀⁻ ion at zero temperature. This includes a proper treatment of the dynamical Jahn-Teller effect, and therefore of the associated orbital angular momentum, of the resulting Ham-reduced gyromagnetic ratio, and molecular spin-orbit coupling. A number of surprises emerge.

First, the predicted molecular spin-orbit splitting is very small, two orders of magnitude smaller than in the bare carbon atom. This is related to the larger radius of curvature of the molecular orbit.

Second, this reduced spin-orbit splitting is now wholly comparable to Zeeman energies, for instance, in X-band EPR at 3.39 KGauss. Hence, a field dependence of the low-temperature susceptibility and of g-factors is predicted, at least in an idealized EPR experiment where additional solid-state effects in the salt or in the matrix could be totally neglected.

Third, we find that the orbital gyromagnetic factor is strongly reduced by vibron coupling, and so therefore are the effective weak-field g-factors for all the low-lying states. The ground state g-factor, in particular, is predicted to be slightly *negative*, about -0.1.

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(**)Email: manini@esrf.fr

(***)Email: gunnar@radix3.mpi-stuttgart.mpg.de

Antiferromagnetic and Ferromagnetic Transitions in pure and doped TDAE-C₆₀ Single Crystals

R. Blinc, P. Cevc, D. Arčon, D. Mihailović, and A. Omerzu
J. Stefan Institute, Jamova 39, 61 111 Ljubljana, Slovenia

The ESR spectra of freshly grown pure TDAE-C₆₀ single crystals show an antiferromagnetic transition around T_N=16 K below which the ESR intensity for H||a at g=2 disappears. SQUID measurements similarly yield a zero value for the spontaneous magnetization in this system. Slightly oxygen doped annealed TDAE-C₆₀ single crystals on the other hand exhibit a weak ferromagnetic transition at T_C=16 K with a small but nonzero value of the spontaneous magnetization as shown by SQUID measurements. The ESR spectra of these crystals show the existence of antiferromagnetic correlations between the unpaired spins on neighboring C₆₀⁻ ions along the c-axis and spin canting which leads below T_C to weak ferromagnetism. This suggests that a Dzyaloshinsky-Moriya type mechanism is responsible for ferromagnetic ordering rather than itinerant ferromagnetism. The temperature dependence of the methyl proton NMR shift here follows above T_C a Curie-Weiss law with a positive Curie temperature T_C=12 K as expected for a case of ferromagnetic transition. Below T_C the internal field at the TDAE protons amounts to 600 Gauss at 6 K. The incomplete orientational ordering of the C₆₀⁻ ions -as seen by the ¹³C NMR- leads to a distribution of exchange coupling constants and significantly influences both the value of T_C and the magnetic properties below T_C. The observation of AFM correlations may help to understand why the same basic molecule, C₆₀, can support such different phenomena as ferromagnetism (in TDAE-C₆₀) and superconductivity (in e.g. K₃C₆₀).

NITROGEN IMPLANTATION IN SOLID C₆₀

T. Almeida Murphy¹, Ch. Wolf¹, Björn Pietzak¹, Th. Pawlik², M. Höhne³, J.-M. Spaeth² and A. Weidinger¹

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³Institut für Kristallzüchtung, Rudower Chaussee 6, 12489 Berlin, Germany

PTu
1

A new paramagnetic center with a prominent hyperfine splitting was found after nitrogen implantation in C₆₀. Electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) were used to characterize the electronic state of this center. The splitting and the isotope effect unambiguously identify this as being due to one nitrogen nucleus. The hyperfine interaction is isotropic, its value is comparable to that of the free nitrogen atom and the spin of the electron system is S=3/2 as in atomic nitrogen. The complex responsible for this center is toluene soluble and stable. We suggest that the complex consists either of nitrogen inside C₆₀ or of nitrogen in a symmetrical position surrounded by C₆₀ molecules.

Analytical high pressure chromatography (HPLC) of the implanted material showed new peaks which have retention times that correspond to a species with a size of three C₆₀ molecules. A correlation between these new species in the HPLC and the paramagnetic center is not obvious since their concentrations are not comparable.

THE FORMATION OF FULLERENE MOLECULES AND UNION-LIKE CLUSTERS UNDER ELECTRON IRRADIATION

F. Banhart, T. Füller, and M. Zwanger

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D-70569 Stuttgart, Germany

PTu
2
Single fullerene molecules such as C₆₀, C₂₄₀, or nested C₆₀@C₂₄₀ as well as larger spherical concentric multi-shell onions are produced by irradiating different modifications of carbon with electrons in a high-voltage electron microscope. The generation process is governed by knock-on collisions of carbon atoms with high-energetic electrons. The temperature of the specimens is not far above room temperature; the whole process is slow and, hence, accessible to direct in-situ observation in the electron microscope. It is observed that *single fullerene molecules* form by a statistic transformation of initially large and irregular carbon cages into spherical molecules. The sputtering of carbon atoms by the electron beam and the capture of atoms from graphitic "substrates", on which the cages adhere, govern the structural evolution of the molecules. The growth dynamics of *multi-shell onions* under different irradiation conditions is studied in detail. The transformation of amorphous carbon into onions proceeds by the formation of instabilities in the amorphous material and a subsequent self-organized development of onions. Spherical carbon onions are only stable under continuous irradiation. Possible reasons for the curling of graphitic planes under electron irradiation will be discussed.

PHOTO CONVERSION OF FULLERENES IN VACUUM USED FOR A PURE CARBON LITHOGRAPHY

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Recently it has been shown by Rao and Eklund that thin solid films of fullerenes are sensitive to UV and visible light and it is known that oxygen plays an important roll in photo reactions of fullerenes. We sublimed fullerenes in vacuum and made films on different substrate materials. Based on spectroscopic data we will compare the light sensitivity of C₆₀ films in oxygen, air and vacuum, using synchrotron and laser radiation from different spectral regions for the photo conversion. Electron and atomic force microscopy have been used for morphological studies. The morphology of the photo converted material and its physical properties depend on the oxygen contamination of the pristine fullerene films and the irradiation conditions.

On the basis of these results we demonstrate a) the feasibility of a pure carbon lithography suitable for processes which require vacuum conditions throughout and b) that photo converted C₆₀ patterns are suitable as resist in the reactive ion etching process of silicon. The resolution limit of the C₆₀ based lithography system is in the sub micron range.

DIAGNOSTICS OF FULLERENE-GENERATING PLASMAS BY OPTICAL EMISSION SPECTROSCOPY

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Abstract

Low-resolution optical emission spectroscopy can be used to detect the fundamental building blocks of fullerene formation in graphite-evaporation plasmas [1-3]. Limitations of this technique like ambiguity of band assignments, moderate sensitivity and the inability to distinguish continuum emission and rotational band structure can be overcome by the use of medium-resolution spectrographs [3].

Using higher resolution it is possible to perform plasma diagnostics like the determination of rotational temperatures of diatomic molecules [1] or the measurement of particle densities from atomic line profiles [4]. Correlation of these parameters with fullerene yield and the properties of fullerene black and electrode deposits will prove helpful in the interpretation of the effects that evaporation parameters like inert gas pressure and arc gap have on the formation of the new forms of carbon.

We present optical emission spectra of fullerene-generating carbon arcs burning in helium and argon atmospheres in a range from 190 to 1000 nm recorded with a spectral resolution < 1 Å. Emissions of atomic carbon of different charges as well as several band systems of diatomic carbon radicals and cyanogen impurities have been detected and analyzed under a variety of conditions.

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EXPERIMENTAL ELECTRON AFFINITIES OF FULLERENES AND THEIR DERIVATIVES.

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Electron affinity is a critical component in the calculations of stability of the fullerene derivatives in which a fullerene is considered as an anionic moiety, particularly in the theoretical calculations of the properties of $M@C_{2n}$ molecules..

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5 In the present report, the available experimental data on electron affinities of fullerenes and their derivatives are reviewed. We also present our latest measurements of the Gibbs energies of the gas-phase fullerene anion/fullerene molecule exchange reactions obtained from equilibrium constant measurements using the Knudsen Cell Mass Spectrometry method.

The new accurate data of the electron affinities (EA) for the series of twenty-one higher fullerenes, include the first EA data for [72]- and [74]fullerenes which are the least stable species in the higher fullerene series. Hitherto, no experimental data on their physical and chemical properties have been published.

The EA values show an increase with the size of the molecule over the whole range, although disruption from the monotonic change was observed in the series of [70]-, [72]-, [74]- and [76]fullerenes, showing [74]fullerene as much stronger electron acceptor than its neighbours [70]- and [76]fullerenes. In principle [74]fullerene can be concentrated in bulk amounts by direct sublimation from the soot and might attract chemists as an interesting new objective in the derivatisation of fullerenes, considering its remarkable reactivity in reduction by a single electron. Our findings of the regularity in the thermodynamic stability of fullerene anions could possibly explain relative stabilities of endohedral metallofullerenes.

CATALYTIC PROPERTIES OF RUTHENIUM FULLERENE COMPOUNDS

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6 In order to evaluate the specific properties of different carbonaceous substances containing fullerenic structural units a series of materials comprising purified C_{60} , raw fullerene black, extracted fullerene black and active carbon was used as support materials for ruthenium.

Hydrogenation of carbon monoxide at atmospheric pressure was used to characterize the catalytic potential of the prepared catalysts under realistic conditions. Due to different sensitivities of the active particle dispersion against heating in reductive atmosphere, significant support effects in the steady state activity vs. temperature behaviour could be observed. At low temperatures the fullerenic materials based catalysts exhibit higher CO conversion rates and higher chain growth probabilities than the active carbon supported catalyst.

1s Surface Shift and Ionization Potential of C60: Screening of Charges in a Molecular Solid

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We have measured the surface core level shift (0.1 eV) and ionization potential (I.P.) of films of varying thickness of C60 deposited on metal substrates. In the thick film limit, the surface core level shift is consistent with calculations of the screening and interaction of charges in C60. The 1s I.P. is reported for solid C60 for the first time, and a previous result for the HOMO I.P. is confirmed. The shift in the HOMO I.P. from gas to solid phase is also consistent with calculations of the screening. We present INDO/CI calculations which show that the 1s hole is screened by a more-or-less uniform depletion of unit charge from the entire molecule, thus essentially equivalent to a valence hole. This has two important implications: 1) the solid state shift of the HOMO should be equivalent to that of the 1s level, thus enabling us to reevaluate the gas phase 1s I.P., and 2) the 1s surface shift should be equivalent to that of the HOMO, implying that analysis of some valence spectra of solid C60 (dispersions, bandwidths, etc.) is probably more complicated than previously acknowledged. The topic of proper reference levels in photoelectron spectroscopy will also be taken up.

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EELS OF FULLERENES AND POLYCYCLIC AROMATIC HYDROCARBONS

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Polycyclic carbon rings are assumed to play a role as precursors in the formation of fullerenes. To investigate similarities of these systems with extended π -electron systems we have performed gas phase EELS measurements on various compounds of the corresponding type of aromatic molecules, the polycyclic aromatic hydrocarbons (PAHs). The single electron excitations and collective excitations (plasmons) up to 30 eV have been measured and are compared to EEL spectra of fullerenes.

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We have used a spectrometer with a position sensitive detector based on a CCD-array. It allows the simultaneous detection of electrons of different loss energies over a range of up to 1.4 eV. The recording time of a spectrum could be reduced by a factor of 50 while keeping the resolution of the spectrometer at 40 meV.

XPS AND XAES STADY OF THE CHEMICAL REACTIONS ON SURFACE FILMS (C60,C60F48)

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X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) are powerful methods for study chemical interaction on a surface of solid state with depth information 1 - 3 nm. The unique possibilities of CKVV Auger spectra of carbon atoms for identification sp²,sp³ and mixture sp²/sp³ states were recognized. The structure XPS of C1s spectra has given chance to calculate stoichiometry of C₆₀F_n and to divide C-F, C=F₂, C-O and C=O interaction. The samples: films C₆₀, C₆₀F_n obtained by vacuum deposition or deposition from solution. The decomposition of C₆₀F_n take place under solution and under electron, ion, ultra-violet irradiation. C₆₀F_n → C₆₀F_{n-m} + mF + m(Cx). The m can be defined from the relation of component C1s spectra. The chemical state carbon atoms Cx are discussed. The data on chemical interaction of C₆₀ with oxygen in air during two years are given.

DOUBLE-PEAK ANOMALY IN ELASTIC RESPONSE OF SOLID C₆₀

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The elastic constant C of pure solid C₆₀ exhibits in the vicinity of order-disorder phase transition at $T_c = 260$ K a qualitatively new type of behavior. Besides the expected negative dip, an additional positive peak appears close to T_c in the real part of C , resulting in what we call a "double-peak" anomaly. The experiments indicate that this effect originates in a slow relaxational process. We present a qualitative description of this behavior, based on macroscopic Landau theory. Extending the Heat-diffusion central peak model, which describes the low-frequency dynamics of phase transitions, with a critically temperature-dependent thermal diffusion time, we attribute the double-peak to a crossover from isothermal to adiabatic behavior and back. The difference between the two limits arises due to a coupling between the fluctuations in order parameter and in temperature.

SIMILARITY LAWS FOR FULLERITE C60

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The crystal fullerite C60 at temperatures exceeding 260 K has the face centered cubic structure. Fullerene molecules in crystal interact each with another through short range potential. So, in its crystal structure the fullerite crystal is similar to rare gas crystals, having the same structural features. The thermodynamical behavior of substances with the mentioned crystal structure is governed by similarity laws in accordance with which the thermodynamical parameters are dimensionless functions of quantities constructed of the temperature T , well depth in the intermolecular interaction potential D and equilibrium intermolecular distance R . One of these similarity laws is used to analyse the measured pressure vapor temperature dependencies for fullerite C60. It permitted to refine the magnitude $D=0.257\pm0.01$ eV known up now with more considerable uncertainty. This magnitude is used for checking the fulfillment of similarity laws for those fullerite thermodynamical parameters for which the experimental data are available. The fulfillment of similarity laws permits to estimate the critical parameters, melting and boiling temperatures, bulk modulus and also Debye temperature for fullerite. On the basis of the data obtained a possibility of existence of fullerene in a liquid state is analysed.

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THE OPTICAL ABSORPTION SPECTRA OF INORGANIC FULLERENE-LIKE MS_2 ($M=Mo, W$)

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Recently, mg quantities of MS_2 ($M=Mo, W$) fullerene-like nanotubes and negative curvature polyhedra (generically called *inorganic fullerene-like material - IF*), were reproducibly obtained from an oxide precursor. The optical absorption spectra in the visible region (400-800 nm) at different temperatures (10-300 K) of IF's were compared with those of the corresponding single crystals. The effect of size, curvature and number of shells was investigated. The well-known excitonic feature of the spectra is retained for all IF samples indicating their semiconductor character. However, the exciton peaks are shifted compared to the single crystal. For large size IF's ($>200\text{\AA}$) a red shift was observed revealing a decrease of the direct band gap. This shift is ascribed to the expansion of the unit cell along the C axis (strain effects). In contrast, the excitons of small size IF's ($<150\text{\AA}$) were blue shifted, indicating an increase of the direct band gap. This shift can be attributed to quantum confinement.

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QUARTIC AND CUBIC ANHARMONIC COUPLING OF A LIBRONIC OSCILLATOR TO A LARGE SET OF INTERNAL MODES

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The quartic and cubic anharmonic interaction of a large set of high-frequency oscillators coupled to one selected low-frequency mode is investigated by the equation of motion method for two-times Green's functions. The model is applied to the interaction of librions (paralibrions) and onball-derived internal modes for C_{60} and Rb_6C_{60} . Available experimental curves obtained in recent inelastic neutron (INS) and Raman scattering studies can be reproduced by strong quartic coupling with respect to the temperature dependence of the linewidths of both type of modes. The T -dependence of the libronic frequencies requires an additional pseudoharmonic contribution. Cubic anharmonicity has been found of less relevance. A disorder induced libronic Debye-like contribution to the low-temperature specific heat is estimated. As a consequence the discrepancy between INS-data and standard specific heat analysis with respect to the Debye-energy can be considerably reduced.

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Thermal hysteresis in DC Resistivity of C_{60} and C_{70} thin films

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We have performed detailed resistivity measurements on thin films of C_{60} and C_{70} , as a function of temperature in the range from 150 K to 450 K. In C_{60} films, a pronounced anomaly at $T_c = 255$ K, in good agreement with the well-known bulk sc to fcc phase transition was observed. In addition, a large difference between heating and cooling curves (hysteresis) was observed. This hysteresis disappears on heating the film above 400 K. C_{70} films show a distinct anomalous behaviour in the temperature range 250 K to 310 K, with large difference between cooling and heating curves. Contrary to previous assumptions, we associate this anomaly with fcc to rhombohedral phase transition shifted about -30 K as compared to the bulk phase transition in C_{70} . This hysteresis also disappeared after heating of the sample above 400 K.

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AN ORDER-DISORDER TRANSITION FOR C60/C70 ALLOY

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We investigated C60/C70 films with a different composition deposited simultaneously on Au and mica substrates from two sources.

The films on mica have been used for X-ray diffraction and those on gold for IR-reflectivity measurements. The X-ray data showed an alloy structure where the lattice parameter scaled with the concentration of C70. A quantitative analysis of reflectivity spectra revealed a dependence of line positions and linewidths on the structure and temperature of the films. A shift of the temperature for the f.c.c-s.c. phase transition was observed.

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STRUCTURE AND OPTICAL PROPERTIES OF C60 THIN FILMS FOR SOLAR CELLS

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A summary is presented of various reasons that lead one to suspect that C₆₀ is an ideal material for the fabrication of high efficiency solar cells. The paper summarizes our first results on experiments performed with C₆₀ thin films. C₆₀ thin films on optical glass and silicon substrates were studied by X-ray diffraction, ESR, Raman and optical transmission spectroscopy.

By varying the deposition conditions we obtain a continuum of structure types ranging from amorphous to crystalline. We find that as the film crystallinity increases the fundamental absorption edge shifts progressively to longer wavelength. This shift implies, that a band gap E_g shifts to smaller values as the degree of crystallinity increases.

Since undoped C₆₀ is an n-type semiconductor, it was decided to deposit C₆₀ film on a substrate of p-type Si and, thereby, produce a heterojunction solar cell. The dark and light I-V characteristics of these devices are presented and an energy band model of heterojunction is discussed.

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STATES SPECIFIC TO SOLID C70

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Recently, it has been suggested that optical properties of fullerenes might be explained in terms of Frenkel excitons (intramolecular) and charge transfer (CT) states (intermolecular). We have already reported evidences for CT states in C60 films. Here, we have extended the study to C70 films. Excitation relaxation and photocarrier generation processes in C70 film have been investigated by means of several spectroscopies at 77K.

The analysis of the luminescence excitation and emission spectra together with the absorption spectrum of C70 film shows that the 0-0 electronic transition is located at 1.83eV. The absorption spectrum retains the characteristic features of C70 molecules (in toluene) except for one band at 2.25eV. The latter is expected to be the signature of the solid state effect. Furthermore, the electro-absorption revealed two distinct modulations at 2.25 and 1.85eV, which are strongly temperature dependent. Moreover, the electric field induced luminescence quenching efficiency increases with increasing the excitation energy above 1.85eV. The photocarrier generation efficiency also shows a sharp increase above 1.85eV and a shoulder at 2.3eV. The concomitant increase of the electric field induced luminescence quenching and photocarrier generation efficiencies above 1.85eV coincide the low energy feature of the electro-absorption.

In the frame work of our previous discussion, we have interpreted these results with branching either in the excitation or relaxation processes involving intermolecular charge transfer excited states (located at 1.85 and 2.25eV). Comparing C70 to C60 films, it is interesting to remark that although the energies of 0-0 electronic transition are similar for C60 (1.85eV) and C70 (1.83eV) films, photocarrier generation thresholds are different: 2.3eV for C60 and 1.85eV for C70. This can be understood because the energies of the lowest CT states of C60 and C70 are 2.3 and 1.85eV, respectively.

MÖSSBAUER SPECTROSCOPY CHARACTERISATION OF IRON BOND TO FULLERENE

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Recently, experimental evidences have been reported for the formation of the strong bonding between iron and fullerene lattice. We have performed Mössbauer spectroscopy experiment for few new iron/fullerene compounds. Starting from C₆₀(ferrocene)₂ compounds, we introduce iron to different positions in fullerene lattice by special thermal treatment and basing on the fullerene protonation. MS proved that in such compounds iron is in Fe(II) or Fe(III) state. MS experiments in various temperatures demonstrate strong Mössbauer parameters fluctuation about T ≈ 258 K for C₆₀Fe₂ on the contrary to the other compounds. The explanations of such properties in the framework of the fullerene libration will be discussed. We will review electronic structure and iron bonding to fullerenes in iron/fullerene family. Possibility of the endohedral Fe@C₆₀ production will be also discussed.

ENERGETICAL AND VIBRATIONAL STUDY OF C₆₀ DIMERS WITH VARIOUS STRUCTURE

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The structure of the C₆₀ dimers in quenched A₁C₆₀ is still an open question. Semiempirical all-valence quantumchemical calculations have been carried out for 6 possible dimer configuration. In four cases there are two bonds between the individual balls and the symmetry of the dimer can be D_{2h} (like in the polymer), C_{2h}, C_{2v} or C_s. In two cases the dimer is only single bonded with C_{2h} or C_{2v} symmetry. Vibrational analysis have been performed for all stable configurations using MNDO, AM1 and PM3 parametrization.

NONLINEAR OPTICAL DYNAMICS AT C₆₀ SINGLE CRYSTAL AND FILM SURFACES

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We discuss the dynamics of second harmonic generation at C₆₀ surfaces upon optical excitation. The most remarkable effect is the fast, efficient, and almost complete suppression of the SH signal. On optical pumping the SHG signal from the samples falls off within our experimental time resolution (45ps) and stays at the low level for times longer than 20ns. It has completely recovered after 50ms. The well reproducible behavior corresponds to a fast integrating light detector which can be read in a SHG process. When the C₆₀ samples are pumped by a UV pulse ($\lambda=355\text{nm}$) the SH signal generated by an IR probe pulse ($\lambda=1054\text{nm}$) decreases to 1/e already at pump densities of $2.8\mu\text{J}/\text{cm}^2$ corresponding to an excitation density of less than one absorbed photon per thousand C₆₀ molecules. We present the efficiency of SHG suppression as a function of the pump beam wavelength between 350nm and 1000nm and discuss the suppression mechanism.

For film thicknesses below 100nm an additional fast decaying component ($\tau=50\text{ps}$) becomes prominent. This component is attributed to the interaction of C₆₀ with the substrate. It constitutes a means to study the coupling of C₆₀ excited states to adjacent dielectric media and metals. We will report on first quantitative measurements of the excitation transfer in the proximity limit (6-20 Å) by making use of Au(111)/alkanethiol/C₆₀ sandwich structures.

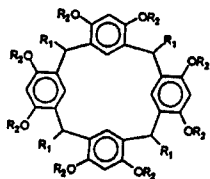
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VOLTAMMETRY OF SUPRAMOLECULAR COMPLEX OF C₆₀ AND CALIX[4]RESORCINARENE UNDECYL DERIVATIVE

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- 1: R₁ = *n*-C₁₁H₂₃; R₂ = H
 2: R₁ = C₆H₅; R₂ = H
 3: R₁ = *n*-C₁₁H₂₃; R₂ = CH₃

Preliminary results are presented on differential pulse voltammetry (DPV) in acetonitrile of a dark-green supramolecular complex (C1) of C₆₀ and calix[4]resorcinarene appended with four *n*-undecyl chains (1). In C1, C₆₀ interacts presumably with alkyl chains of 1 because no complex is formed in case of 2. In contrast to six one-electron reversible DPV peaks for C₆₀, there are only two DPV peaks for C1: reversible one at *E*_{p1} = -0.90 V vs. Ag/AgCl, and ill-defined one at *E*_{p2} = -1.30 V. Most likely, either the C₆₀⁻ monoanion formed at the first electroreduction is released from C1red or it reacts with hydroxyl groups of 1 to yield an electroinactive product. In order to verify the latter, an attempt was made to use 3 instead of 1. However, 3 is insufficiently soluble both in acetonitrile and other polar aprotic solvents.

C60 DERIVATE FILMS: EPITAXIAL GROWTH, PHOTOEMISSION AND ANGULAR-RESOLVED INVERSE PHOTOEMISSION STUDIES

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We have investigated the electronic structure of new group of fullerene derivatives, synthesized by photochemical reaction and purified by column chromatography on silica gel. Thin films of C60-(C2NH)-2(COOCH3), C60-(C2NH)-2(COOCH2CH3), and C60-(C2NH)-2(COOCH3C6H6) were grown in UHV by sublimation onto in situ cleaved GeS(001) and clean Au(110)(1x2) substrates and the epitaxial character of the films was verified through the observation of sharp hexagonal LEED patterns. Clear differences depending on the functional group can be observed in the valence band spectra taken with different photon energies, and the deviations from the pure C60 spectral weight are larger for larger *hν*. A strong effect of the functional groups on the electronic structure is seen also comparing the dispersion of the unoccupied electronic states as measured by inverse photoemission in pure and functionalized C60.

SPECIFIC PROBLEMS ENCOUNTERED DURING THE REACTION OF CARBANIONS WITH C_{60} IN POLAR SOLVENTS

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It is well known that charged nucleophiles such as carbanions are able to open double bonds on the C_{60} . We have recently shown that up to 6 "living" polystyrene can be added to this fullerene in toluene, a common non polar solvent of both reactives. But the synthesis of other well defined architectures (pearl necklaces, networks ...) requires the use of difunctional "living" polymers which can only be obtained in polar solvents like THF. The reaction between carbanions and C_{60} in such a polar solvent, where C_{60} is insoluble and electron transfer is favored, is more complicated. We have shown that despite the use of a large excess of carbanions, only 3 "living" polystyrene chains can be covalently bound onto C_{60} . That results from a competition between addition reaction and electron transfer. By using carbanions of various reactivities, we were able to determine the conditions under which the addition reaction is favored or pure electron transfer occurs.

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ORIENTATIONAL ORDERING TRANSITIONS IN FCC AND HCP C_{70} SINGLE-CRYSTALS

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Despite a large effort, considerable uncertainty still exists concerning the number and location of orientational ordering transitions in the face-centered-cubic (fcc) and hexagonal (hcp) modifications of solid C_{70} . Using high-resolution capacitance dilatometry between 200 and 400 K, we have investigated these transitions in C_{70} single crystals with both fcc and hcp morphologies. Expansion measurements were made along two different [111] directions and a [110] direction of the fcc crystal, and both parallel and perpendicular to the hexagonal c-axis of the hcp crystal. Upon heating, we observe three first-order transitions in both types of crystals (for fcc at ~ 304 K, ~ 355 K and ~ 365 K; for hcp at ~ 285 K, ~ 303 K and ~ 367 K). Upon cooling, three transitions are observed in the fcc crystals (at ~ 340 K, ~ 310 K and ~ 302 K), while the hcp crystal undergoes four transitions (at ~ 335 K, ~ 310 K, ~ 302 K and ~ 280 K). The 335 K-transition upon cooling (hcp) occurs only in the high-T phase. These results may indicate that the present understanding of the orientational ordering transitions in solid C_{70} is inadequate.

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ORIENTATIONAL FLUCTUATIONS, DIFFUSE SCATTERING AND ORIENTATIONAL ORDER IN SOLID C₆₀.

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Starting from a microscopic model of interactions between C₆₀ molecules on a fcc lattice, we formulate the orientational interaction potential in terms of symmetry adapted rotator functions. All irreducible representations of the cubic group up to the manifold $l = 12$ are taken into account. We introduce new symmetry adapted normal coordinates for orientational motion. Physical quantities such as the free energy are formulated in terms of these normal coordinates. We calculate the diffuse scattering law throughout the Brillouin zone. The theory describes in a very satisfactory way recent X-ray and neutron scattering experiments. We study the orientational order parameter taking into account all T_{2g} and T_{1g} representations up to the manifold $l = 10$. The temperature evolution of the order parameter is obtained within molecular field theory from the selfconsistent solution of a transcendental equation. The coupling of representations largely enhances the transition temperature and the first order character of the phase transition.

ON THE STABILITY OF THE JAHN-TELLER DISTORTED STATES OF C₆₀ AND SMALLER FULLERENES

Károly Németh, Mihály Kállay, Péter R. Surján

Dept. Theor. Chem., Eötvös University H-1518 Budapest 112, POB 32, Hungary

The stability of Jahn-Teller distorted states of C₆₀ and some smaller fullerenes (e.g. C₂₀) are analysed by the XHuge-model. The excited state potential surface of C₆₀ exhibits several critical points, which have been located previously. The Hessian matrix analysis shows, however, that most of them are saddle points and only D_{5d} ³A_{2g}; D_{3d} ³A_{1g}; D_{5d} ¹A_{2g}, ¹A_{2u}; D_{3d} ¹A_{1g} and ¹A_{2u} can be assigned to local minima. The analysis of the C₂₀ cluster shows that its ground state is degenerated and distorts. However the the ionized C₂₀²⁺ is stable (icosahedral) while its excited states are Jahn-Teller active. The results suggest that C₂₀²⁺ is more stable then the neutral molecule. Zero-field splitting parameters (D and E) and spin-densities of the triplet states of several clusters are calculated.

Tuesday, March 5

45

Cis-1-Bisimino-[60]fullerenes: Opening of the Fullerene Core and Fragmentation to $C_{59}N^+$

Georg Schick and Andreas Hirsch

Institut für Organische Chemie, Henkestr. 42, 91054 Erlangen, Germany

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For further investigations of the regioselectivity of addition reactions to C_{60} we synthesized [6,6]-bridged bis-iminofullerenes by allowing the fullerene to react with azidoformates at elevated temperatures. From these reactions we obtained the first regioisomeric bisadducts with organic addends having a *cis-1*-addition pattern. The addition pattern of these green fullerene derivatives was determined by ^{13}C NMR-spectrometry using ^{15}N -labelled compounds. Interestingly, these are the first fullerene derivatives with an open [6,6]-bridged structure. Under the conditions of FAB-mass spectrometry these *cis-1* adducts fragment very efficiently to the heterofulleren ion $C_{59}N^+$.

**COMPUTATIONS OF 19 IPR ISOMERS OF C_{86}
AND 35 IPR ISOMERS OF C_{88}**

Zdeněk Slanina^{a,*}, Shyi-Long Lee^a, Mitsuho Yoshida^b, and Eiji Ōsawa^b

^aDepartment of Chemistry, National Chung-Cheng University, Chia-Yi 621, Taiwan

^bDepartment of Knowledge-Based Information Engineering,
Toyohashi University of Technology, Toyohashi 441, Japan

C_{86} allows for nineteen IPR structures, six of them having a C_2 symmetry (the structures are labelled 1-19 as introduced in a previous study; the C_2 species are 1, 4, 5, 9, 17, 18). According to recent results of Y. Achiba *et al.* just two species appear in NMR spectra of C_{86} , both of C_2 symmetry. The species 17 is found as the ground state of the C_2 subset in MM3, AM1, SAM1, *ab initio* HF/STO-3G and HF/3-21G calculations. If temperature effects are considered through rotational-vibrational partition functions, the isomer 9 comes as the second particularly stable species (though it is not the second lowest in potential energy); the last mentioned species is located, e.g., about 97, 144, and 145 kJ/mol above the 17 structure in the MM3, AM1, and SAM1 calculations, respectively. The 9/17 equimolarity is computed close to 3000 and 4000 K by the MM3 and SAM1 treatment, respectively. Similar computational study is also reported for 35 IPR isomers of C_{88} .

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Theoretical study on Frenkel excitons in solid C_{60}

László Udvardi

Quantum Theory Group, Institute for Physics, TU Budapest
H-1521 Budapest, Budafoki út 8, Hungary

The optical spectrum of the isolated C_{60} molecule has been compared to the local excitations of the solid system, where the effect of the intermolecular interactions in the crystal has been treated by means of perturbation theory. The excitonic band structure and density of states has been determined for FCC and simple cubic structures. The change of the properties of the excitations has been investigated in different order of the multipole expansion and the perturbation theory. The model applied in the study is based on the CNDO/S parametrization of the Hamilton operator. The theoretical results has been compared to the experiments.

FORMATION AND ORIGIN OF "SHELL" ON C_{60}

K.Yamanaka¹, N.Kino¹, M.Ozawa¹, J.Li¹, K.Kisio¹, K.Kitazawa¹
M.S.Kim² and H.Koinuma²

¹Department of Applied Chemistry, The University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan

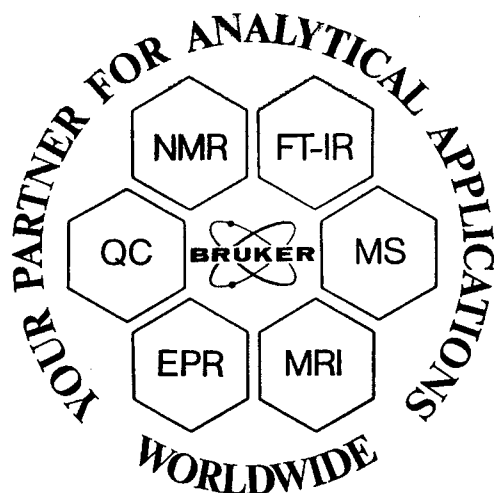
²Research Laboratory of Engineering Materials, Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

A shell skeleton structure was observed to remain after a C_{60} crystal, exposed to light and air, was sublimated under vacuum. The shell was yellowish to transparent in the color and was not soluble in aromatic solvents.

In order to know the origin and structure of the shell, we examined relatively the formation of the shell under vacuum, air, inert gas, pure oxygen gas, and wet inert gas with or without UV-light irradiation.

We also performed structural analyses by TEM, X-ray diffraction, Raman scattering, microscopic FT-IR spectra and TOF-MS (time-of-flight-mass spectroscopy). FT-IR spectrum showed no C=O bond absorption at about 1700cm^{-1} . We observed dimer, trimer and tetramer in the TOF-MS spectrum. But each mass number of the peaks was not a multiple of 720 a.m.u but was a multiple of about 720 (15~35) a.m.u.

Discussion will be made on these observations.



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Applications

- 8:30 – 9:30 S. STAFSTRÖM, Linköping University, Linköping, SE
Superhard and Elastic Carbon Nitride Films With a Fullerene-like Microstructure
- 9:30 – 10:00 R.H. BAGRAMOV, Res. Center for Superhard Materials, Troitsk, RU
Manufacturing of Superhard and Ultrahard Materials from C₆₀ Fullerite. Extrimely Low Heat Capacity of Dence Fullerites
- 10:00 – 10:30 Coffee break
- 10:30 – 11:00 D. MIHAILOVIĆ, Josef Stefan Institute, Ljubljana, SLO
Self-assembly of Fullernes in Solution and in Solid Form: A Study of Polymerized and Micellar Forms of C₆₀ and C₇₀
- 11:00 – 11:30 M. BALOOCH, University of California, Livermore, USA
The Interaction of Fullerenes with Surfaces
- 11:30 – 12:00 P. GRUEN, Argonne National Laboratory, USA
- 12:00 – 17:00 Mini Workshops
- 17:00 – 18:30 Dinner

Chemistry of Fullerenes

- 18:30 – 19:00 A. HIRSCH, Inst. für Organische Chemie, Erlangen, BRD
New Aspects of Organic Chemistry of Fullerenes: Tectons and Heterofullerenes
- 19:00 – 19:30 J.MATTAY, University of Münster, BRD
Progress in Fullerene Chemistry: From Exohedral Functionalization to Heterofullerenes
- 19:30 – 20:00 M. PRATO, Dipartimo di Scienze Farmaceutiche, Trieste, I
Synthesis and Chiroptical Properties of Fullerene Derivates
- 20:00 – 20:30 L. DUNSCH, Inst. für Festkörperforschung, Dresden, BRD
ESR spectroscopic studies of the spin state and electron transfer at endohedral fullerenes

Special Poster

- 20:30 – 21:00 *Special Poster*

SUPERHARD AND ELASTIC CARBON NITRIDE FILMS WITH A FULLERENE-LIKE MICROSTRUCTURE.

H. Sjöström, S. Stafström, M. Boman, and J.-E. Sundgren
Department of Physics, Linköping University
S-581-83 Linköping (Sweden)

Thin carbon nitride films with a composition varying in the range $\text{CN}_{0.2}\text{-CN}_{0.3}$ were prepared using reactive magnetron sputtering of graphite in pure nitrogen discharges. The mechanical properties of these films were obtained from nanoindentation measurements. An elastic recovery of around 90% was obtained and the hardness (H) and elastic modulus (E) were ~60 and ~200 GPa, respectively. These values lie between those of diamond (H=100, E=1050 GPa) and TiN (H=20, E=600 GPa). The microstructure of the films contain buckled and curved graphite like planes. Calculations of equilibrium structures of nitrogen containing systems showed that the fullerene-like buckling can be explained in terms of the formation of pentagons, which is energetically more favourable in the presence of nitrogen than in the presence of carbon only. *Ab initio* delta-SCF calculations of the N1s and C1s core levels indicated that a fraction of the carbon atoms are sp^3 hybridized, like in diamond. Based on this result we propose a cross linked structure with sp^3 hybridized bonds between the graphite like basal planes to explain the hardness of the material.

MANUFACTURING OF SUPERHARD AND ULTRAHARD MATERIALS FROM C_{60} FULLERITE. EXTREMELY LOW HEAT CAPACITY OF DENSE FULLERITES.

V.D.Blank, R.H.Bagramov, G.A.Dubitsky, S.G.Buga

Research Center for Superhard Materials. 142092, Troitsk, Moscow region, Russia.

Heat capacity (C_p) of fullerite C_{60} treated with high pressure and temperature is represented. High pressure (up to 130 GPa) and temperature (up to 2000 K) treatment has been provided with so-called 'thoroid' device. Specific media to provide shear deformation inside 'thoroid' device have been designed. C_p was measured with differential scanning microcalorimeter (actual heat rate was 2 K/min). Results are represented in comparison to graphite and diamond measured.

Fullerite C_{60} bulk P-T treated samples transform to a number of phases, most of the phases being different to diamond and graphite. Some of the samples exhibit superhardness with no diamond phase presented. Some of them have hardness higher than diamond do [1].

C_p of C_{60} without treatment was found to be in good agreement with data available.

C_p temperature dependence for a number of treated with high temperature and pressure C_{60} samples have been measured. C_p of some samples is even lower than that of natural diamond. Correlation between hardness, specific weight, X-ray structure and heat capacity have been found. Possible interpretation of the results is under discussion.

SELF-ASSEMBLY OF FULLERENES IN SOLUTION AND IN SOLID FORM:
A STUDY OF POLYMERIZED AND MICELLAR FORMS OF C₆₀ AND C₇₀.

D. Mihailovic, A. Mrzel, A. Hassanien, A. Omerzu and I. Muševič
Jozef Stefan Institute, Jamova 39, Ljubljana, Slovenia

In the first part of the talk, an atomic force microscope study of the C₆₀ polymer properties will be presented, analyzing force constants and distorted structures that form on unoriented and (111)-oriented epitaxial fullerene films as a result of illumination by laser light.

10:30
APPL
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In the second part we will report for the first time a study of nano-micellar fullerene structures in solution. Under certain conditions micellar structures encapsulate fullerene molecules in such a way that they are chemically protected from their surroundings. Similar coatings are also found to self-assemble on fullerene thin films, crystals or powders, affording protection from organic solvents and reagents that normally attack the fullerene cage. New chemistry opportunities are demonstrated using the micellar encapsulation as a protection of only the fullerene part of the molecule enabling addition reactions to appended groups. Using the different properties of different fullerene micellar structures a simple environmentally friendly route for fullerene separation is also demonstrated.

The Interaction of Fullerenes with Surfaces*

M. Balooch and A. Hamza

University of California
Lawrence Livermore National Laboratory
Livermore, California 94550

The interaction kinetics of C₆₀, C₇₀, and C₈₄ with Si, SiO₂ and graphite are studied by Modulated Molecular Beam Mass Spectrometry (MMBMS), Temperature Programmed Desorption (TPD), and Scanning Probe Microscopy. The accommodation coefficient, sticking probability, activation for desorption and the stability of these molecules on surfaces are discussed. The angular distributions of scattered molecules are determined.

11:00
APPL
4

The selective growth of SiC films on Si(100), Si(111) and vicinal surfaces are studied by Low Energy Electron Diffraction (LEED). The mechanical properties of the film (hardness, elastic modulus and friction coefficient) are determined by a modified atomic force microscopy. The work function of the film grown is studied by Ultraviolet Photoelectron Spectroscopy (UPS) and Kelvin probe and are compared with clean Si. The effect of oxygen and water vapor exposure on the work function are determined.

*This work was supported by the U. S. Department of Energy, at Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

Wednesday, March 6

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11:30
APPL
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New Aspects of the Organic Chemistry of Fullerenes: Tectons and Heterofullerenes

Andreas Hirsch

Institut für Organische Chemie, Henkestr. 42, 91054 Erlangen, Germany

18:30
CHEM
1

Regioselective additions to C_{60} provide the opportunity to tailor design stereochemically defined architectures ranging from molecules with a "normal" size up to monodispers nanostructures. In these systems the fullerene core serves as structure determining tecton. On the other hand regioselective additions to C_{60} are the key steps for the modification of the fullerene framework itself, like the formation of ring-opened derivatives and heterofullerenes.

PROGRESS IN FULLERENE CHEMISTRY: FROM EXOHEDRAL FUNCTIONALIZATION TO HETEROFULLERENES

Jochen Mattay, Johannes Averdung, Heinrich Luftmann¹, Ingo Schlachter¹, Christina Siedschlag and Gregorio Torres-Garcia.

Institute of Organic Chemistry, University of Kiel, D-24098 Kiel, Germany.

¹ University of Münster, Germany

1. Exohedral Functionalization

Within a few years, fullerenes have become an established compound class in organic chemistry. Among the huge variety of functionalization, cycloadditions have always played an important role. In this report we will discuss various examples of (cyclo)additions to (60)fullerene. Typical examples of exohedral functionalizations from our laboratory are the following:

- pyrrolofullerenes from 2H-azirines
- aziridinofullerenes and oxazolofullerenes from acylnitrenes
- aziridinofullerenes and azafulleroids from azides
- cyclohexanofullerenes from 1,3 dienes by Diels-Alder reaction
- hydroxyalkyl-dihydrofullerenes via C_{60} -radicals cations by oxidative electron transfer.

2. Aza-dihydro(60)fullerene

A new approach to produce heterofullerenes is described. Starting from a fullerene with an intact cage which is activated by suitable exohedral functionalization, aza-heterofullerene is generated in the gas phase under DCI mass-spectrometric conditions. On the basis of AM1-calculations the 1,2-closed structure is proposed to be the most stable one.

19:00
CHEM
2

SYNTHESIS AND CHIROPTICAL PROPERTIES OF FULLERENE DERIVATIVES

Tatiana Da Ros and Maurizio Prato*
Dipartimento di Scienze Farmaceutiche
Piazzale Europa 1, 34127 Trieste, Italy

Alberto Bianco, Claudio Tonioio, Fabiola Novello, Michele Maggini, and
Gianfranco Scorrano
Centro di Studio sui Biopolimeri and Centro Meccanismi di Reazioni
Organiche del CNR, Dipartimento di Chimica Organica,
Via Marzolo 1, 35131 Padova, Italy

19:30
CHEM
3

The 1,3-dipolar cycloaddition of azomethine ylides to C_{60} is a valuable method for the functionalization of fullerenes.^{1,2} Depending on the reactants used to generate the reactive 1,3-dipole, either fulleropyrrolidines or fulleroproline derivatives can be obtained. In the case of fulleroproline derivatives, a proline ring is fused on a 6,6-ring junction of the fullerene spheroid. This unnatural amino acid can be manipulated under standard coupling conditions to afford fulleroproline-containing peptides. In circular dichroism spectra, all optically active fulleroproline derivatives and peptides display a wide range of active bands, due to the large window of absorptions of the fullerene moiety coupled with the dissymmetric perturbation induced by the chiral Pro ring. The most distinctive feature in the CD spectra of these compounds is a sharp maximum at about 428 nm. The sign of this Cotton effect offers a strong clue to the determination of the absolute configuration of the newly-generated Pro chiral $C\alpha$ atom: a positive maximum is associated with R configuration, whereas the S isomer gives a negative maximum.

ESR SPECTROSCOPIC STUDIES OF THE SPIN STATE AND ELECTRON TRANSFER AT ENDOHEDRAL FULLERENES

20:00
CHEM
4

LOTHAR DUNSCH, ANTON BARTL and UWE KIRBACH
*Institut für Festkörperforschung, IFW Dresden e. V., Abt. Elektrochemie und
leitfähige Polymere, Helmholtzstraße 20, D-01069 Dresden (Germany)*

This work is concentrated on the spin state of endohedral fullerenes including scandium, yttrium, lanthanum, cer, praseodymium, samarium, europium, holmium, thulium and lutetium as metals in the carbon cage. The ESR spectroscopic properties were studied in organic solutions at room and lower temperatures. It is shown that well resolved ESR spectra in solution are found for several metals indicating both the free spin of the carbon cage, structural informations on different fullerene species and the orientation of the metal ion inside the cage. By in situ ESR spectroscopy in electrochemical reactions of those endohedral fullerenes the change of the spin state is demonstrated. The effect of the electron transfer on the fullerenes is discussed in comparison to that of fullerene derivatives.

CHEMICAL REACTIVITIES OF ENDOHEDRAL METALLOFULLERENES

Takeshi Akasaka*Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan.*

Shigeru Nagase and Kaoru Kobayashi

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan

Sp
1 Since the first proposal in 1985, endohedral metallofullerenes (fullerenes with metal(s) inside the hollow spherical carbon cage) have been prepared and characterized. Recent progress toward isolation and purification of endohedral metallofullerenes has been achieved and some of their physical properties have been reported. None of their chemical properties, however, has been explored. Here we describe the first chemical derivatization of endohedral metallofullerenes such as La@C₈₂ and Gd@C₈₂ giving the corresponding exohedral adducts. Some of interesting salient features of endohedral metallofullerenes are discovered. Although disilirane does not add thermally onto the empty fullerenes such as C₆₀ and C₈₂, a facile thermal addition to La@C₈₂ takes place. Chemical reactivities of endohedral metallofullerenes will be discussed on the basis of their electronic properties.

Pulse ESR/ENDOR on the Polymer Phase of Rb₁C₆₀M. Bennati, U. Krüger, G. Denninger, A. Grupp and M. Mehring*2. Physikalisches Institut, Universität Stuttgart
Pfaffenwaldring 57, D-70550 Stuttgart, Germany*

Sp
2 The polymer phase of Rb₁C₆₀ has been discussed in terms of a low dimensional metal. The corresponding conduction electron ESR signal consists of a Lorentzian line, which broadens with increasing temperature characteristic for a metallic system. However, in our pulsed ESR measurements we find two different spin contributions, one connected with conduction electrons (only FID: free induction decay) and the other with localized spins (spin echo). Their different temperature dependence will be discussed. Moreover we performed double resonance experiments (ENDOR/Overhauser Shift) which again show different hyperfine interactions for the localized and conduction electrons with ^{85,87}Rb and ¹³C. The impact of these observations for understanding the physical properties of the polymeric phase will be presented.

Characterization of nanosize metallic particles encapsulated in carbon nanostructures

W.K. Maser^a, P. Bernier^a, P. Molinie^b and S. Lefrant^b, P.M. Ajayan^c

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^cMPI für Metallforschung, Seestraße 92, 70174 Stuttgart, Germany

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Carbon nanotubes and nanosize particles can be produced during the electric arc-discharge process using a graphite cathode and a graphite anode containing additionally one or more elements of the periodic table. In this work we are using different stoichiometric mixtures of yttrium (lutetium), nickel, and boron and will focus especially on the magnetic properties of the nanosize particles. Investigating the inner core of the cathodic deposit by HRTEM, we see that metal nanoparticles can be encapsulated inside multi-walled nanotubes, as well as in polyhedral carbon nanoparticles. In both cases the metal nanoparticles appear to be highly crystalline. Additionally, nanosize metal particles can also be found embedded in more glassy carbon. Those particles are more spherical and they seem to be more amorphous. X-Ray diffraction shows that, in all cases, the samples do not contain simple metals or metal carbides, but form intermetallic compounds. SQUID measurements on those samples reveal interesting magnetic properties which are related to the metallic nanoparticles. Depending on the used mixtures in the anode, the properties can range from diamagnetic to paramagnetic behaviour with magnetic hysteresis. A superconducting transition at 15 K for the Y-Ni-B mixture is observed as well. Temperature and magnetic field dependencies on the different samples will be discussed

NMR EVIDENCE FOR 1D ANTIFERROMAGNETIC FLUCTUATIONS IN Rb_1C_{60} AND Cs_1C_{60}

V. Brouet¹, H. Alloul¹, Y. Yoshinari¹ and L. Forro²

¹Physique des Solides, UA2 CNRS, Université de Paris-Sud, 91405 Orsay (France).

²Laboratoire de Physique des Solides Semicristallins, IGA, EPFL, 1015 Lausanne (Switzerland).

It is by now well established that the A_1C_{60} compounds display an orthorhombic (o)-phase below room temperature, where the C_{60} balls form polymerized chains in the a direction. Yet the consequences of this strongly one dimensional (1D) structure on the symmetry of the electronic properties of these systems are still debated. The exact nature of the transition at low-T in Rb_1C_{60} and Cs_1C_{60} is also still unclear. We have performed ^{13}C NMR measurements on the three phases of A_1C_{60} ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) and alkali NMR in Cs_1C_{60} (^{133}Cs) and Rb_1C_{60} (^{87}Rb). We show that in K_1C_{60} , T_1 behaves as in an ordinary 3D metal ($T_1 T = \text{cst}$), while for Rb_1C_{60} and Cs_1C_{60} , T_1 is nearly constant from 50 K up to room temperature. The comparison with the relaxation on the alkali allows us to attribute this behavior to strong antiferromagnetic fluctuations, which are well described by a highly correlated 1D spin chain model.

NMR data confirms the occurrence of a magnetic transition at about 25 K in the Rb and Cs polymers. Unlike μSR , which favors a highly disordered magnetic state, our data suggests that the low-T state is antiferromagnetic (AF) in a spin flop state at the applied NMR field, with relatively large local moments ($m = 0.5 \mu_B$) AF coupled along a chain.

How a Lanthanum Atom Moves inside a Fullerene:

Ab-initio Molecular Dynamics

Wanda Andreoni¹ and Alessandro Curioni^{1,2}

¹IBM Research Division, IBM Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

²Scuola Normale Superiore, I-56014 Pisa, Italy

Sp
5 Many static calculations exist on metallofullerenes. Understanding the type of bonding is sometimes tricky and has needed ab-initio approaches in the past. The issue of the dynamics of a metal atom inside a fullerene is still unresolved. We shall present the results of ab-initio molecular dynamics calculations, which provide a new picture, and show the limitations of static approaches. Comparison with experiments so far available is also made.

PULSE ESR/ENDOR INVESTIGATION OF HYPERFINE INTERACTION IN $M@C_{82}$ ($M=Y, La$)

S. Knorr, A. Grupp and M. Mehring

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A. Bartl and L. Dunsch

IFW Dresden e.V., Helmholtzstraße 20, D-01069 Dresden, Germany

Sp
6 We report on pulsed ESR and ENDOR investigations of $La@C_{82}$ and $Y@C_{82}$. By using different techniques like electron spin echo envelope modulation (ESEEM) and electron nuclear double resonance (ENDOR) we were able to determine the hyperfine interaction of ^{139}La , ^{89}Y and ^{13}C with the electron spin residing on the C_{82} cage. The hyperfine interaction in frozen solution is compared with that in the liquid state.

In addition we have investigated the g-shift tensor of $Y@C_{82}$ in frozen solution at different temperatures. The temperature dependent lineshapes and the corresponding spin relaxation rates provide information about the dynamics of the C_{82} cage.

OPTICAL SPECTRA OF A_1C_{60} SALTS

K. Kamarás and S. Pekker

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P. O. Box 49, Budapest, Hungary H 1525

D. B. Tanner

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L. Forró

Département de Physique, École Polytechnique Fédérale de Lausanne, Lausanne,
Switzerland CH-1015Sp
7

We will present a group theoretical analysis of allowed infrared lines in the monomer, dimer and polymer phase of AC_{60} . If we restrict ourselves to a molecular model without crystal-field corrections, the monomer is expected to show four lines as in pure C_{60} , whereas 66 IR-active transitions are allowed in the polymer and 132 or 174 in the dimer, depending on symmetry (D_{2h} and C_{2h} , respectively). We compare our measured infrared spectra of RbC_{60} single-stoichiometry powder with these predictions. In addition, the visible transmission of the polymer phase will be shown for both RbC_{60} powder and KC_{60} crystalline fibers. The peaks in the near infrared/visible/UV region show considerable broadening from pure C_{60} , indicating a metallic band structure. These peaks exhibit no anisotropy in the KC_{60} fibers, because the morphological directions do not coincide with the chain axes.

POLYMERISED FULLERITE PHASES

Marques L.*[†], Nuñez-Regueiro M.[§], Hodeau J.-L.** Laboratoire de Cristallographie, CNRS, associé à l'Université Joseph Fourier,
BP 166X 38042 Grenoble, France.

§ EPM-Matformag CNRS 166X 38042 Grenoble France.

Solid fullerite presents at normal temperature and pressure a face centered cubic structure (fcc) where C_{60} molecules are freely rotating, center to center molecules separation is 10\AA . At 255K these molecules develop an orientational order reducing the structure symmetry to a simple cubic one. We report here that heating under high pressure in a belt apparatus drives C_{60} to new distorted crystalline phases, which are essentially characterised by two nearest molecules distances $\sim 10\text{\AA}$ and $\sim 9.2\text{\AA}$.

We show that at least three new polymerised phases could be obtained [1]: a rhombohedral and a tetragonal phases which contains, respectively, hexagonal and nearly quadratic polymerised layers, and a orthorhombic phase containing linear polymerised chains. The excellent agreement with theoretical calculations [2], show that these new carbon phases can be understood as the long range order polymerisation of C_{60} . Pressure-temperature phase diagram and synchrotron powder diffraction patterns of these new phases will be presented.

Sp
8

LIBRATIONS AND VIBRATIONS OF AC_{60} : NEUTRON AND IR STUDIES

Michael C. Martin and Peter Wochner *Brookhaven National Laboratory, Laszlo Forro EPFL Switzerland*, Daniel Koller and Laszlo Mihaly *Department of Physics, SUNY @ Stony Brook*

Inelastic neutron scattering and mid-infrared transmission measurements were performed in a quest for a further understanding of the inter-fullerene interactions in the monomer, dimer, and polymer structural states of monoalkali fullerenes. Elastic neutron structural data confirmed the unit cell doubling in the quenched dimer phase. Librational modes were measured as a function of temperature and are compared between the polymer and dimer structures. We find evidence for different types of bondings. IR measurements are also used to show the different symmetry states of the various structural phases; additional activity of vibrational modes due to the lower symmetry structures can be used to pinpoint the energies of many silent modes. We also explore the phases produced when very rapid quenching to below liquid nitrogen temperatures is performed.

Work at BNL supported by the U.S. Department of Energy, contract #DE-AC02-76CH00016; work at Stony Brook supported by NSF Grant DMR9202528.

SILICON CARBIDE FORMATION FROM C_{60} FILMS ON SILICON

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SiC films on Si have been prepared by depositing C_{60} films on silicon and annealing them between 800 - 900°C. To prevent loss of C_{60} by evaporation, annealing was performed by facing two substrates to each other, confining C_{60} between the two plates of Si. The reaction of silicon with C_{60} to give SiC is very slow at 700°C and requires longer than 100 min. However, 100 min. at 800°C results in continuous SiC films and only traces of the C_{60} can be detected on the surface. At 900°C a shorter annealing time can form continuous and uniform SiC films. An additional way to confine C_{60} is by treatment with a beam of Ar^+ with energy in the keV range. This treatment transforms the surface layer of C_{60} into a nonvolatile carbon deposit, which then acts as a capping layer during the annealing process. By rastering the ion beam, we can write a chosen pattern on the C_{60} film. Upon increasing the temperature to 300-350°C, the C_{60} film evaporates off the unbombarded surface, while it remains only in the areas that were irradiated. In the irradiated zones the modified C_{60} layer confines the underlying C_{60} on the silicon surface during the annealing, allowing the formation of SiC, by processing at 900°C for 300 min. At shorter times, traces of the modified capping layer are visible at the edge of the irradiated zone. Our preliminary results demonstrate the principle of fabricating SiC structures on silicon without masking and etching processes and with the high lateral resolution possible with ion beams.

PREPARATIONS OF PRISTINE AND Ba-DOPED C₆₀ FILMS BY HOT WALL EPITAXY

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The Hot-Wall-Epitaxy (HWE) allows to grow epitaxial layers very close to thermodynamic equilibrium, which is very essential in the case of Van der Waals epitaxy of fullerenes. The semiclosed nature of the HWE reactor provides a growth regime at high vapour pressures without loss of source material and offers the possibility to dope the epilayers or to form compounds during growth. The successful growth of C₆₀ epilayers was further improved by a post-growth in-situ annealing process. In a series of experiments, the annealing time and temperature was varied between 10 and 60 minutes and 120°C and 150°C respectively. The optimal crystalline property was found for an annealing time of 20 minutes at 130°C. The crystalline quality was analysed by high resolution X-ray diffraction and X-ray pole figure studies which showed an FWHM of the (111) reflex of 140 arcsec.

An additional Ba source was used in the HWE reactor to dope the C₆₀ layers and to grow Ba_xC₆₀ films. The Ba source could be heated separately so that the vapour pressure of C₆₀ and Ba could be controlled independently. The substrates of glass and (100) oriented mica were preheated for one hour at 420°C before the growth process in the same vacuum chamber at a background pressure of 2.10⁻⁷ mbar. The Ba doped layers were prepared in a thickness range between 0.5 and 80 µm. The growth rate was mainly controlled by the Ba source temperature and varied between 0.22 Å/s and 31 Å/s for Ba temperatures in the range of 470°C to 750°C.

To measure the electrical properties of the Ba_xC₆₀ layers, which are not stable on air, it was necessary to install electrical contacts at the sample holder, for resistivity measurements during growth. Four Au contacts were evaporated before growth on the substrates which allowed a continuous measurement of the resistance during growth. After the growth, the thickness of the Ba_xC₆₀ layers was measured and the resistivity evaluated. A clear decrease of the resistivity with increasing of Ba incorporated in the C₆₀ layers was observed with a saturation value of 4.10⁻⁴ Ωcm. We assume, that the lowest resistivity was obtained for Ba₆C₆₀.

Sp
11Structure refinements on the dimer phase of Rb₁C₆₀

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A metastable phase of Rb₁C₆₀ develops below 270 K, when the formation of polymers is prevented by rapid cooling. The structure of this phase is nearly orthorhombic but it was shown [1,2] that a monoclinic superstructure is constructed from dimerized C₆₀ molecules.

It was argued [2] that dimerization is the result of covalent bonding but the type of the intermolecular bond could not be established. Structure solution from x-ray powder diffraction data was impeded by the large unit cell and low symmetry of the dimer phase and the coexistence of a yet unidentified other phase. Recently single phase samples were obtained with the aid of a special heat treatment. After mapping out molecular orientations we were able to determine the space group and establish the type of dimer bond but the exact intramolecular geometry is still to be determined.

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PREPARATION AND MAGNETIC PROPERTIES OF HAFNIUM AND ZIRCONIUM FULLERIDES

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C₆₀ is known to form complexes with some metallocenes, for example ferrocene. Furthermore, it was reported that iron fulleride was obtained by decomposition of ferrocene with appropriate temperature gradient in vacuum glass tube. Basically same procedure was applied using other metallocenes in order to synthesize series of transition metal doped fullerides. Up till now, zirconocene dichloride and hafnocene dichloride fullerides were obtained, even though non-reacted-C₆₀-free complex has not been achieved. Both of the final products show positive χ values (about 1.5×10^{-5} emu/g at 1000 G: hafnium fulleride) almost constant for temperature change. In addition, phase transition was observed at about 130K in case of hafnium fulleride, and the initial curve had a hysteresis below the transition temperature.

Mean-field studies of surface orientational melting in crystalline C₆₀

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and INFN - Istituto Nazionale per la Fisica della Materia

Oriental melting transitions at the surface of a molecular crystal are less commonly studied than their positional counterpart. A recent and striking example is the C₆₀ crystal whose surface disorders at a temperature 30 K lower than the bulk [1]. Systems which exhibit a first-order bulk transition can develop wetting by the disordered phase at the surface, i.e. the transition is initiated by the first surface layers. The observed disordering at the surface of the C₆₀ is an important signal in this direction. However, the surface transition found in C₆₀ is clearly first-order, which could not easily be anticipated. In order to understand this transition, we have performed a number of mean field calculations with different models: firstly, with a four state Potts model; then, we added in the intermolecular coupling a dependence from the lattice expansion, then again surface outwards relaxation and also anharmonic terms. However, none of these ingredients was capable of explaining the surface transition.

Presently, we are carrying out a new mean field analysis using a realistic intermolecular potential of the kind proposed by Lamoen, Michel *et al.*[2]. This potential correctly predicts the fine orientational structure at low temperatures.

The results of this new calculation will be discussed at this meeting.

OPTIMIZATION OF PREPARATION OF EPITAXIAL β -SiC LAYERS FORMED BY FULLERENE-CARBONIZATION OF SILICON

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Deposition of C_{60} and C_{70} fullerenes at moderate temperatures between 700°C and 1000°C enables the formation of epitaxial β -SiC layers on (001)- and (111)-oriented silicon. This low temperature and easily controllable deposition process might be important for applications of silicon carbide in high temperature and high power microelectronics as well as for the use of SiC as hardcoating and passivation material.

Structure, topography and composition of these β -SiC-layers is studied by X-ray diffraction (XRD), X-ray pole figure measurements, atomic force microscopy (AFM) and Rutherford backscattering spectrometry (RBS). The quality of the layers is extremely sensitive to the substrate temperature, the kind of evaporated fullerene molecule and the orientation of the substrate. The influence of the film thickness on the structure is investigated.

Depending on the process parameters the thickness of these SiC-layers varies between 50 nm and 1.5 μ m. Their morphology is characterized by a high concentration of defects (e. g. twins). The formation of silicon carbide layers at low temperatures is determined by the diffusion of the silicon towards the surface and the energy resulting from the fragmentation of the fullerenes.

ELECTRONIC STRUCTURE OF THE TWO C_{78} ISOMERS WITH C_{2v} SYMMETRY

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The two C_{78} isomers with C_{2v} symmetry have been separated by multi-cycle HPLC purification. The electronic structure of these isomers has been studied in solution using infrared absorption and in the solid state using electron energy-loss spectroscopy in transmission and photoemission spectroscopy. We show that both the occupied and unoccupied density of states as well as the energy gap are considerably different for the two isomers although they both possess the same molecular symmetry.

ELECTRON-PHONON COUPLING SIGNATURES IN VIBRATIONAL SPECTRA OF ADSORBED FULLERENE MONOLAYERS

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G.P. Williams, NSLS, Brookhaven National Laboratory, Upton, NY 11973.

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Based on recent IRRAS and HREELS results on C_{60} and C_{70} monolayers adsorbed on bare and alkali-covered Ag(111) and Au(110) surfaces electron-phonon coupling will be discussed: in the HREELS spectra we find evidence for resonant effects in the interaction of the incoming electron with intramolecular vibrations of the fullerene molecule. Moreover the $T_{1u}(2)$ and the $T_{1u}(4)$ modes of C_{60} show an enhancement of oscillator strength which is interpreted on the basis of recent ab-initio calculations(1) in terms of the charge transfer from the substrate to the adsorbate. In the IRRAS spectra of $C_{60}/Ag(111)$ we find a new IR line due to the breaking of the symmetry at the silver surface and for $C_{60}+K/Ag(111)$ a strong antiabsorption feature with a Fano line profile shows up at 1450 cm^{-1} . The origin of this peak is discussed in terms of an anomalous skin effect(2).

Ferromagnetic versus molecular ordering in C_{60} charge transfer complexes

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Tetrakis(dimethylamino)ethylene was the first and so far the only C_{60} CT complex, which exhibits molecular ferromagnetism with a Curie temperature of about 16 K. A lot of work was presented dealing with $C_{60}[TDAE]$, but a convincing access to the origin of the low temperature phase is still missing. A second approach to an understanding of the ferromagnetism in C_{60} CT complexes is by electro crystallisation of C_{60} radical anion salts. We try to do chemical engineering by a variation of the counter ions. We will show that one of them - $C_{60}[P(C_6H_5)_4]_2$ - is an excellent model system, since it exhibits a lot of the features which are typical for solids and solutions containing C_{60} anions, though magnetic ordering is missing. The main advantage is the availability of single, air stable crystals. We will present NMR, EPR, conductivity and susceptibility measurements in $C_{60}[P(C_6H_5)_4]_2$ and $C_{60}[TDAE]$. We find a rich variety of molecular and spin dynamics with characteristic temperature domains and a universal behaviour for the C_{60} mono anions. At high temperatures we have an isotropic g-tensor. Fast rotation of the C_{60} anion is found in solid state NMR of ^{13}C , ^{111}In and ^{31}P . The rotation is "frozen out" at about 170 K in clear contrast to C_{60} NMR. At about 140 K the EPR shows a pronounced, temperature dependent g-factor anisotropy. We suppose, that the 3 fold degeneracy of the C_{60} SOMO is lifted by a change of the undoped C_{60} conformation, and we find a transition from a dynamic high temperature Jahn-Teller distortion (with a spherical C_{60} anion, I_h symmetry) to a static low temperature Jahn-Teller distortion (Rugby shaped C_{60} anion, D_{5d} or D_{3d} symmetry). The transition is accompanied by a molecular ordering of the distorted C_{60} anions, which is the precursor to the magnetic ordering in $C_{60}[TDAE]$. The proposed spin-glass behaviour of this compound is the consequence of orientational disorder of the C_{60} anions.

ON THE NATURE OF THE CHEMICAL BONDS BETWEEN THE MONOMERIC UNITS OF THE FULLERENE POLYMER

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Experimental and theoretical evidences show that unusually long carbon-carbon bonds ($r_{CC} > 1.6 \text{ \AA}$) exist in the $(C_{60})_2$ dimer as well as in the fullerene polymer $(C_{60})_x$. The possible consequences of such long bonds on the electronic structure are discussed. Another interesting point is the rectangular nature of the bonds resulting from the 2+2 cycloaddition. These features may, in principle, prevent the applicability of simple one-electron models. However, the sophisticated quantum chemical calculations we have performed do not show any strange behavior of the electronic system at the bonding region, and the role of electron correlation seems not to be essential. This encouraged us to carry out a detailed theoretical study on the electronic structure of these systems using simple molecular orbital and density functional models.

Energy weighted electron density maps are compared with experimental STM images which show a charge accumulation *between* the fullerene cages in $(C_{60})_x$. A simple model for the theoretical rationalization of the STM results is developed and the role of solvent effects is discussed.

PHASE TRANSITIONS DURING ANNEALING OF RBC60 AFTER QUENCHING

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Single crystal single phase RbC60 was prepared by doping C60 at 420 K. The crystal was subsequently quenched from 405 K to 80 K within 7 minutes. The change of structural details was then studied by taking Raman spectra during the annealing process up to room temperature. After quenching the response from the monomer is retained with a contamination of an orthorhombic phase. Above 170 K new features are observed in the spectra which are not consistent with extended chains connected by four membered rings. Finally, at room temperature the well known features of the orthorhombic phase are observed.

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In addition the doping process for Rb-doping at temperatures below the fcc-o phase transition was studied. Doping was observed to lead directly to a phase separated state between Rb3C60 and C60. This means the o-phase can not be reached directly by doping from the gase phase.

COMBINED EXAFS AND XRD STUDY OF $C_{60}(IBr)_x$

J. Dumschat¹, S.N. Kolesnik^{1,2}, G. Nowitzke^{1,3}, H. Werner³, D. Herein³,
W. Bensch⁴, Yu.S. Grushko^{2,3}, R. Schlögl³, and G. Wortmann¹

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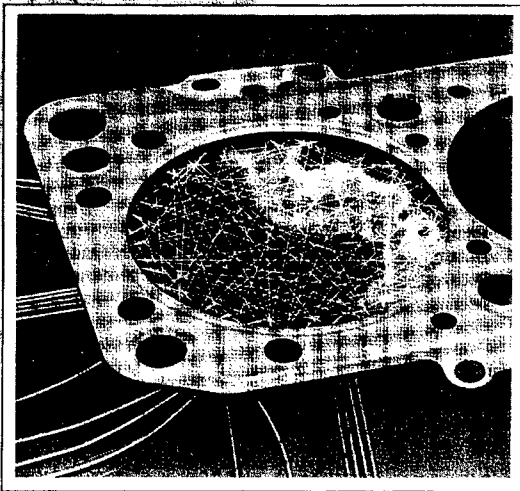
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(3) Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin-Dahlem, Germany

(4) Institut Anorganische Chemie, Universität Frankfurt, D-60439 Frankfurt/Main, Germany.

The structural arrangement and the chemical nature of IBr molecules intercalated in a C_{60} matrix were studied by x-ray diffraction (at 300 K) and by x-ray absorption (EXAFS and XANES) at the bromine K-edge as well at the iodine K- and LI-III-edges (in the range 20 K - 300 K). From XRD analysis a tetragonal structure with $a = 9.923(3)$ Å and $c = 34.40(1)$ Å is derived; the EXAFS analysis provides complementary information about the structural arrangement of (only slightly modified) IBr molecules. From the analysis of the EXAFS Debye-Waller factors we derive information about the molecular dynamics pointing to an order-disorder transition in the intermolecular IBr arrangement around 276 K (similar to the melting transition of the halogen sublattice in the corresponding graphite intercalation compounds [1]) and being observable also in DSC measurements.

[1] W. Krone et al., Synth. Met. 29, F247 (89). - Support by the DFG (Wo209/10, 436 RUS)



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A_xC_{60}

- 8:30 – 9:00 J. E. FISCHER, Materials Sc. Dep. and Lab. for Research on the Struct. of Matter, University of Pennsylvania, USA
Synthesis and Properties of Mixed Alkali-Alkaline Earth Fullerides
- 9:00 – 9:30 P. PETIT, Institut Charles Sardon, Strasbourg cedex, F
ESR Contribution to the Study of Normal State Properties in Alkali Fullerides
- 9:30 – 10:00 G. Zimmer, Universität Stuttgart, BRD
 ^{87}Rb and ^{13}C NMR of Rb_3C_{60} in The Superconducting State
- 10:00 – 10:30 Coffee break
- 10:30 – 11:00 G.A. SAWATZKY, University of Groningen, NL
Influence of Longer Range Coulomb Interactions in C_{60} -Compounds and Overlayer
- 11:00 – 11:30 P. RUDOLF, Faculte Universitaires N.-D. de la Paix, Namur, B
Electronic Structure Study of K_xC_{60} Compounds With $x > 6$
- 11:30 – 12:00 S. MODESTI, TASC-INFN, Trieste, I
Electronic Structure of Endohedral La_xC_{60} compounds
- 12:00 – 17:00 Mini Workshops
- 17:00 – 18:30 Dinner

Endohedral Fullerenes

- 18:30 – 19:00 M. M. KAPPES, Universität Karlsruhe, Karlsruhe, BRD
Spectroscopic Probes of High Fullerene Isomers: Filled vs. Empty Cages?
- 19:00 – 19:30 K. P. DINSE, Technische Hochschule Darmstadt, Darmstadt, BRD
EPR Investigation of Metallo-Endofullerenes
- 19:30 – 20:00 R. TELLMANN, Max Born Institut, Berlin, BRD
Production and Characterisation of Macroscopic Amounts of Alkali-Metallofullerenes

Poster session II: fullerides, endohedral fullerenes, related materials

Synthesis and Properties of Mixed

Alkali-Alkaline Earth Fullerides

J. E. Fischer

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An important new class of fullerides is obtained by mixed alkali-alkaline earth intercalation. We targeted $\text{MBA}_2\text{C}_{60}$ ($\text{M} = \text{K}, \text{Rb}$ or Cs) and $\text{MBA}\text{CsC}_{60}$ to isolate the effect of molecular valence on electronic structure, while maintaining the crystal structure of known alkali metal-fulleride superconductors typified by M_3C_{60} . We describe the chemical reasoning which led to these compounds, and the novel techniques by which they were realized. X-ray diffraction and Raman scattering show that these are face-centered cubic with pentavalent and quadrivalent C_{60} 's respectively, and are thus isostructural with K_3C_{60} and its binary and ternary analogs. We find no evidence for superconductivity down to 0.5 K, while the density of states at the Fermi energy is at least 10 times smaller than that of K_3C_{60} . ^{13}C NMR indicates strong dynamical disorder above room temperature, which may be related to the anisotropic crystal field induced by cations of different valence.

8:30
 A_xC_{60}
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ESR Contribution to the Study of Normal State Properties in Alkali Fullerides.

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Elliot expression for conduction electron ESR linewidth is given by: $\gamma\Delta H_{1/2} = 1/T_1 = \alpha(\Delta g)^2/\tau$; where T_1 is the spin lifetime, α is a metal dependent constant of the order of unity, Δg is the g shift from the free electron value and τ the electron-phonon scattering time. Elliot showed that Δg is a function of λ : $\Delta g \sim \lambda/E$, where E is the energy separation between the considered band and the nearest band with the same transformation properties. This relation has been experimentally verified by Beunee and Monod for normal metals. Rewriting Elliot expression as $1/T_1 = \alpha(\Delta g)^2\rho$, where ρ is the electrical resistivity, the experimental determination of Δg allows to compare the ESR linewidth to the electrical resistivity, and we are no longer obliged to estimate an ambiguous parameter such as λ/E .

We report our ESR results of the temperature variation of both linewidth and Δg for three compounds: $\text{Na}_2\text{CsC}_{60}$, K_3C_{60} and Rb_3C_{60} . The temperature dependence of $\Delta H/(\Delta g)^2$ reproduces surprisingly well that of the electrical resistivity reported so far for K_3C_{60} and Rb_3C_{60} . The conclusion that may be drawn from these experiments is that Elliot-Yafet model applies for A_3C_{60} , a conductivity mechanism originated by electron-electron scattering may be definitely ruled out.

We also report the variation of the density of states $n(E_F)$ for the three compounds as a function of lattice parameter a . Our results are compared to theoretical works and show a steeper dependence of $n(E_F)$ vs a than those generally reported and substituted in McMillan formula.

9:00
 A_xC_{60}
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^{87}Rb AND ^{13}C NMR OF Rb_3C_{60} IN THE SUPERCONDUCTING STATEG. Zimmer, M. Mehring, F. Rachdi*, J. E. Fischer[†]

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[†]Department of Materials Science and Engineering,

University of Pennsylvania, Philadelphia, Pennsylvania 19104

9:30
 A_xC_{60}
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Concerning the electronic properties, the superconducting state of Rb_3C_{60} is of particular interest. When interpreting the NMR results, different physical phenomena have to be discussed. The electronic susceptibility vanishes in the superconducting state, therefore effects on the line position and the line width can be observed. On the other hand, the vortex lattice and its dynamics lead to an additional frequency shift and line broadening. An estimation of the penetration depth as well as of the pinning potential will be presented. In addition, off center dynamics of the octahedral anion will be considered for the interpretation of the NMR parameters.

In order to distinguish between these different phenomena, relaxation rates and the spectra were analyzed as function of the magnetic field. T_1^{-1} and T_2^{-1} relaxation rates reflect dynamical processes which are discussed in terms of off center dynamics of octahedral anions and vortex dynamics. The second moment of ^{87}Rb and ^{13}C lines can be modelled by the vanishing Knight shift anisotropy and vortex broadening at low temperatures.

10:30
 A_xC_{60}
4H. Tjeng, J.v.d. Brink, G. Sawatzky

University of Groningen, NL

Influence of longer range coulomb interactions in
C60 compounds and overlayers.

ELECTRONIC STRUCTURE STUDY OF K_xC_{60} COMPOUNDS WITH $x > 6$

P. Rudolf, Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultes Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium.

A. J. Maxwell, P. A. Bruhwiler, S. Andersson and N. Martensson, Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden.

We present Cls X-ray absorption and photoemission results for K_xC_{60} with $x > 6$, the so-called 'superfullerides'. These are the first measurements of the unoccupied valence band for these systems and confirm that more than six electrons can be transferred to each fullerene. We observe saturation of the K-to- C_{60} charge transfer, with part of the t1g LUMO+1 orbital remaining unoccupied, so that fewer than 12 electrons are accepted per C_{60} molecule. This fullerene state exhibits metallic behaviour, while a transition to insulation behaviour is observed as lower charge states are formed by adding more C_{60} . The superfullerides appear to follow the pattern of strongly correlated solids.

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 A_xC_{60}
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ELECTRONIC STRUCTURE OF EXOHEDRAL La_xC_{60} COMPOUNDS

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A possible route to the formation of new C_{60} compounds is the epitaxial growth of structures by controlled evaporation of C_{60} and metals in UHV on well ordered substrates. Materials that cannot be prepared by more conventional techniques, such as the diffusion into bulk C_{60} of atoms with low diffusion coefficients, can be grown with by this technique. We have grown exohedral La_xC_{60} compounds by alternating well ordered monolayers of C_{60} and submonolayers of La. The geometric, electronic and vibrational structure of these compounds have been studied by low energy electron diffraction, photoemission, Auger and high resolution electron energy loss spectroscopy. The C_{60} sublattice remains well ordered, while the La sublattice has no long range order. Each La atom transfers 2 electrons to the C_{60} cage, the third La valence electron remaining localized on the La atoms. The La charge state differs from the calculated values for endohedral $La@C_{60}$ (3+), but is in agreement with a recent calculation for exohedral LaC_{60} . La_xC_{60} is a small gap insulator for $x < 3$ and a metal for $x > 3$. The metallic compounds have the states derived from the LUMO+1 partially filled. The occupied density of states shows a large broadening of the C_{60} derived structure due to hybridization with the metal states, similar to the situation in Ca_xC_{60} and Ba_xC_{60} .

11:30
 A_xC_{60}
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SPECTROSCOPIC PROBES OF HIGH FULLERENE ISOMERS: FILLED VS. EMPTY CAGES?

Rudi Michel¹, Dirk Fuchs², Eva Werner¹, Hans Eisler¹, Sabine Richard¹, Frank Hennrich¹, Carolin Lehner³, Marianna Fanti⁴, Francesco Zerbetto⁴ and Manfred M. Kappes¹

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Abstract.

Microcrystalline samples of C₇₆, C₇₈(C_{2v}'), C₇₈(C_{2v}'), C₇₈(D₃), C₈₀(D₂), C₈₂, La@C₈₂ and Y@C₈₂ have been studied via laser photoacoustic, Raman and FT-IR methods. A preliminary systematization of the observations will be attempted.

EPR-Investigation of Metallo-Endofullerenes

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Production and separation techniques for Metallo-Endofullerenes have been optimized to such an extent that comparative studies of various Metallo-Endofullerenes in different solvents are now feasible. The aim of our current studies is the elucidation of the spin dynamics of paramagnetic Endofullerenes. From an analysis of the temperature dependence of EPR linewidth, important conclusions about the correlation time of fluctuating magnetic fields and electric field gradients at the site of the ion can be derived. In particular, the question is addressed if molecular tumbling motion or internal hopping of the ion are dominant sources of spin relaxation. By comparing the contribution of fluctuating nuclear quadrupole interaction in La@C₈₂ and Sc@C₈₂, we could determine the relative quadrupole interaction in both radicals. We found that the e²qQ/h value of Sc@C₈₂ can be rationalized by simply scaling the La-value by the Sternheimer anti-shielding factor of the tri-positive ions, thus suggesting identical electric field gradients at the respective ion site. Furthermore, the amount of charge transfer from the metal ion to the carbon shell is still unknown. From a comparative study of Me@C₈₂ (Me = Sc, Y, La) of the ¹³C-hfs couplings we conclude that in all these cases the charge transfer seems to be practically equal. Finally we report about the EPR properties of three new isomers of La@C₉₀.

PRODUCTION AND CHARACTERISATION OF MACROSCOPIC AMOUNTS OF ALKALI-METALLOFULLERENES

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We have developed a new method of producing macroscopic amounts of endohedral Li, Na and perhaps K and Rb fullerenes. This is done by exposing fullerene monolayers deposited by an oven to an alkali ion beam during the deposition process. The resulting substance is characterized by laser desorption mass spectrometry (LDMS), Raman, Far Infrared and other methods. The product is shown to be stable in air, at least for some months.

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The energy dependence of the alkali ion incorporation is comparable with previous gas phase experiments carried out by Anderson et. al. in 1992. Comparison shows, that the data obtained in our experiments corresponds to the sum of the endohedral substances and all their fragments as measured in the gas phase.

The presentation will deal with the specific production conditions for the alkali metallofullerenes and with the characterization of the substances. In addition to the LDMS results, we will place emphasis on the comparison of the Raman and Far Infrared Spectra with the existing theoretical work. Also first results of solubility and purification experiments will be reported.

Proton NMR in a TDAE-C₆₀ Single Crystal

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PT_h 1 The temperature dependence of the methyl proton NMR shift of a TDAE-C₆₀ single crystal follows above T_C a Curie-Weiss law with a positive Curie temperature T_C ≈ 12 K as expected for the case of a ferromagnetic transition. Below T_C the shifts are proportional to the magnetization and saturate below 10 K. The internal field at the TDAE protons amounts at 6 K to 600 Gauss and exceeds by an order of magnitude the internal field determined by electron spin resonance at the C₆₀⁻ ions. The result shows that in addition to the direct C₆₀⁻-C₆₀⁻ interactions which seem to be of antiferromagnetic nature a part of the exchange coupling between the C₆₀⁻ ions is mediated by the TDAE⁺ groups. It is this indirect coupling which might give rise to the Dzyaloshinsky-Moriya term in the spin Hamiltonian which is responsible for weak ferromagnetism in this system.

C-13 ELECTRON SPIN RESONANCE AT ENDOHEDRAL FULLERENES IN SOLUTION

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PT_h 2 Today endohedral metallofullerenes can be prepared in macroscopic quantities and successfully characterized by ESR spectroscopy used in connection with the mass spectrometry.

The aim of this contribution is to study the endohedral fullerenes of lanthanum, yttrium and scandium in solution with respect to their electronic states of the cage using C-13 ESR satellite spectra.

The hyperfine structured ESR spectra of isolated metallofullerenes La@C₈₂, Y@C₈₂ and Sc@C₈₂ have the metal redox state of 3⁺ and show well resolved ¹³C satellites in the ESR spectra. There exist five groups of electronically different C-atoms in the C₈₂ cage. Using quantum chemical methods the electronic structure of the charged fullerene cage is studied by the spin density distribution calculated by a LCAO-DFT-procedure.

MAGNETOTRANSPORT PROPERTIES OF THIN FILMS OF ALIGNED CARBON NANOTUBES

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We report Hall coefficient (R_H) and magnetoresistance ($\Delta\rho/\rho$) measurements on thin films of aligned carbon nanotubes. R_H is positive in the whole temperature range (1.7-300 K) showing the predominance of hole transport in the electronic conduction. The upper limit of the carrier concentration is $1.6 \times 10^{19} \text{ cm}^{-3}$. The $\Delta\rho/\rho < 0$ suggests a noncoherent transport between the nanotubes.

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SEARCH FOR DEVIATIONS FROM THE IDEAL STRUCTURE OF Rb(3)C(60)

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We have carried out an x-ray powder diffraction study of a phase-pure sample of the superconducting alkali-fulleride Rb(3)C(60) with measurements at $T=20\text{K}$, 35K , 295K , 460K and 590K . Its structure is well known to be cubic (space group $\text{Fm}\bar{3}\text{m}$) with $a=14.43\text{\AA}$ (at 295K). Rietveld refinements of this model clearly yield less than unit occupancy for the tetrahedral Rb site at $(1/4, 1/4, 1/4)$, while confirming full occupancy of the octahedral site at $(1/2, 0, 0)$. This results in a total refined stoichiometry of Rb(2.90)C(60) . Other samples prepared away from the nominal stoichiometry of 3 also refine to a deficient tetrahedral occupancy, even for a sample containing some Rb(4)C(60) . Previous 87-Rb NMR measurements have shown 3 lines below $T=443\text{K}$, although the structural model has only 2 different Rb sites. Given the extremely large thermal parameter of the octahedral Rb, this has led to speculation that this atom is displaced from the center of its position below that temperature. We have searched for evidence of such an off-center displacement of this atom. From the refinement of structural models with different amounts and directions of displacement from the $(1/2, 0, 0)$ position we can conclude unambiguously that there is no such displacement at any temperature. Indeed, a comparison of data taken below and above $T=443\text{K}$ does not show any evidence of structural change associated with the disappearance of the third 87-Rb NMR line. Finally, it has been suggested that there may be a structural change associated with the superconducting transition at $T_c=29\text{K}$. Comparing spectra with $T=20\text{K}$ and $T=35\text{K}$ we fail to see any such change.

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ANION RADICALS OF [60]-FULLERENES. (EPR STUDIES)

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[60]-Fullerene mono-anion was originally described with a broad EPR line having peak-to-peak (pp) larger than 5 mT, and g-value 2.000 [1]. It has been additionally characterized with a band in VIS/near-IR at 1075 nm. Now, we applied various *in situ* reduction techniques (quenching of the photoexcited fullerene with triethylamine [2], photoreduction in TiO₂ suspensions [3], as well as cathodic reduction) in diluted solutions, and observed very narrow [60]-fullerene mono-anion EPR line **A** with $pp_A = 0.09$ mT and $g_A = 2.0000$. The so formed mono-anion **A** transfers easily electron to oxygen under the formation of superoxide mono-anion, and the released fullerene can be again reversibly reduced to the mono-anion **A**. With the progressing reduction mono-anion **A** converts to its consecutive product **B** characterized with still narrower EPR line, $pp_B = 0.042$ mT and $g_B = 2.0006$ [2,3]. After stopping the reduction, radical **B** is converted backwards to radical **A**. Radical **B** is probably di-anion or an associated form of mono-anion. Similar radical products showed also ortho-quinodimethane adducts of [60]-fullerene [4]. Various forms of [60]-fullerene mono-anion found by EPR imply the formation of its variously associated structures.

ESR Study of Annealed and Freshly Grown TDAE-C₆₀ Single Crystals: Interplay Between Antiferromagnetic and Ferromagnetic Ordering

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The low temperature magnetic properties of freshly grown and annealed TDAE-C₆₀ single crystals have been studied with ESR. In some freshly grown crystals the ESR signal intensity disappears at 6 K demonstrating the onset of singlet type antiferromagnetic ordering. In annealed crystals on the other hand a ferromagnetic ordering takes place around 16 K resulting in a tremendous increase in the ESR signal intensity at a and b parallel to H₀, as well as in powder samples but not for c||H₀. This demonstrates that the basic correlations between the electron spins on neighboring C₆₀ ions along the c-direction are of AFM type and that the Dzyloshinski-Moriya interaction and spin-canting are probably responsible for the weak ferromagnetic ordering.

HIGHLY EFFICIENT METHOD OF FULLERENES AND METALLOFULLERENES PRODUCTION IN CARBON PLASMA JET AND THEIR PROPERTIES INVESTIGATION

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Installation for production of fullerenes and metallofullerenes based on carbon plasma jet was designed. The plasma jet is spontaneously blown at the pressure of inert gas nearly equal to atmospheric pressure, flow rate having been 2 liter per minute in the closed cycle. Productivity of the installation amount to 2 gram per hour of fullerenes, it contents of the deposited soot reaching 20 %. These findings were obtained by electronic absorption spectra and the direct weight methods. But most remarkable, the installation gave excellent results for generation of metallofullerenes such as $Gd_k@C_{2n}$ and $Tb_k@C_{2n}$. The content of metallofullerenes in the mixture of fullerenes preliminary filtered through Al_2O_3 was no less than 10 % as documented by EPR spectroscopy. Fine structure of EPR spectra pointed out that atoms of metal were trapped inside the fullerene cage and displaced from a center. The optical absorption spectra showed the fading of spectra in the long-wavelength area, but short-wave area remained the same. The similar fading of spectra in the long-wavelength area was observed in the literature for spectra of absorption from other metallofullerenes (for instance $Sc@C_{84}$).

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DOPING INDUCED PHOTOCONDUCTIVE BEHAVIOUR INDUCED BY C60 IN AN INSULATING POLYMER MATRIX

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The polymer Poly[C-{(4-N-dimethylamino)phenyl}]dithienylmethine is anon-conjugated polymer which has a conductivity of 10-14S/cm. However, upon doping the polymer, it is possible to alter its intrinsic nature and fabricate a Schottky contact with Al. The dopant species in this case is C60. The device shows good stable rectifying behaviour. The absorption spectrum is also altered significantly, the bandgap being altered from 2.4 eV to 1.9 eV: There is also an appearance of a cationic induced absorption peaking at 1.7 eV, this being due to the doping C60 species. When undoped the polymer shows no detectable photoconductive behaviour. However when doped the polymer shows substantial current increases when illuminated. There is no evidence of degradation of the current or photocurrent at constant low fields.

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ELECTRON SPIN RESONANCE DEPENDENT PHOTOCONDUCTIVITY OF UNDOPED POLYCRYSTALLINE C₆₀ AND C₇₀ FILMS

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9 Photoconductivity detected magnetic resonance (PCDMR) experiments combine the technique of electron spin resonance spectroscopy with the investigation of the electron transport in semiconductor samples.

Spin dependent photoconductivity measurements were performed to obtain detail information about charge carrier transport in fullerenes. Undoped polycrystalline C₆₀ and C₇₀ films were prepared by sublimation and connected to coplanar Au contacts. The photoconductivity of these films under white light from a halogen source was measured during *B* field sweep in a cw X-band electron spin resonance spectrometer.

The signals observed show narrow (~ 4 G) lines with complicated structure. The dependencies of the line shapes and the effective *g*-values on temperature, microwave power, applied voltage and on the sample illumination intensity and wavelength are described and discussed.

CHROMATOGRAPHIC ELUTION BEHAVIOR OF ENDOHEDRAL METALLOFULLERENES: INFERENCES REGARDING EFFECTIVE DIPOLE MOMENTS

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Chromatographic retention relationships between endohedral metallofullerenes and a [2-(1-pyrenyl) ethyl]silyl-silica stationary phase were studied in detail and are discussed in comparison with those of empty fullerenes. The elution behavior of metallofullerenes reflects the polar nature of these molecules and allows inferences regarding the presence of a dipole moment in these species.

Furthermore the dipole moment of La@C₈₂ was investigated by direct dipole moment measurements in solution. These results are consistent with preliminary results obtained from retention relationships.

ELECTRON SPECTROSCOPY STUDY OF RARE-EARTH (Eu,Yb) ATOMS
INDUCED MODIFICATION OF C_{60} FULLERITE ELECTRONIC STRUCTURE

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It has been proposed recently that rare-earth elements can be used for formation of fullerides with unique properties, including superconductivity. In this report C_{60} fullerite electronic structure evolution under doping by rare-earth (Eu,Yb) atoms is discussed. Auger electron spectroscopy and Auger electron appearance potential spectroscopy were used to reveal the changes of carbon-derived density of occupied and unoccupied electronic states respectively during Eu(Yb) adsorption onto C_{60} film and thermal annealing of formed systems. Energy loss spectroscopy measurements were performed to clarify the mechanism of Eu(Yb)/ C_{60} phases formation. It has been shown that similar to the case of alkaline-earth fullerides, formation of Eu(Yb)/ C_{60} compounds is accompanied by partial filling of C_{60} unoccupied orbitals and hybridization phenomena have to be taken into account. The changes of carbon-derived density of electronic states during Eu(Yb) graphite intercalation compounds formation are discussed for comparison.

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THE SYNTHESIS AND CHARACTERISATION OF OLIGOMERIC C_{60} OXIDES

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The dimeric compound $C_{120}O$ has been obtained in preparative quantities through the coalescence reaction of C_{60} and $C_{60}O$. Here we report on the chemical transformations of $C_{120}O$ powder during heating in an inert atmosphere. All products were characterized by analytical HPLC and matrix-assisted TOF MS. Two main trends can be observed: first, the formation of oxidized C_{60} oligomers and, second, the redecay of $C_{120}O$ back into C_{60} . With regard to the C_{60} oxide oligomers we detected in the temperature range 200-500°C the preferable formation of $C_{120}O_2$ (two isomers) and $C_{180}O_3$ (several isomers). Traces of $C_{180}O_2$, $C_{180}O_4$, $C_{180}O_5$, and some compounds with modified cage structure were also found. At temperatures higher than 500°C we observed C_{119} in the MS of the reaction mixtures. However, so far we could not isolate this odd-numbered species using chromatographic procedures. Nevertheless we believe that the occurrence of the large odd-numbered fullerene C_{119} indicates the possibility of producing higher fullerenes from C_{60} and its oligomeric oxides.

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GAS-PHASE OXIDATION OF MULTISHELL NANOTUBES AND NANOPARTICLES: KINETICS AND MORPHOLOGY CHANGES

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PT_h 13 It is well known that gas phase oxidation of carbon multishell nanotubes and nanoparticles formed in the cores of cathode deposits results in an opening of the nanotubes' tips and in enrichment of material with nanotubes due to preferential oxidation of nanoparticles.

We observed that on isothermal oxidation of deposit cores at 700 °C structural changes occur in the nanotubes in competition with oxidation of the tips. Multishell tubes are transforming gradually at heating to curved graphitic strips, as evident from HRTEM study.

Kinetics of gas phase oxidation of deposit cores with oxygen reveals two stages, as it was shown recently also for fullerene black [1]. Both stages are Arrhenius-type, but with different preexponents.

DTGA and DSC studies reveal two irreversible transformations at 640 K and 690 K and one reversible one at 820 K. Possible reasons of this two stage kinetics are discussed.

[1]. M. Wohlers, A. Bauer, Th. Rühle, F. Neitzel, H. Werner and R. Schlögl, *J. Full. Sci. Technol.* (1996), in press

WAVELENGTH SELECTIVE DESORPTION OF C₆₀

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PT_h 14 Desorption of C₆₀ from the surface of a C₆₀ single-crystal is studied using a Free Electron Laser ('FELIX' user facility, FOM Rijnhuizen, Nieuwegein, The Netherlands). This laser produces a train of IR pulses (pulses of ps duration, ns's apart during a 'macro'-pulse of several μs) and can be tuned over the 100–2000 cm⁻¹ range. C₆₀⁺ ions are produced either directly by the IR laser or via single-photon post-ionization of the desorbed neutrals. The ions are then mass selectively detected in a linear Time-Of-Flight (TOF) setup.

The C₆₀⁺ ion intensity shows a strong dependence on the wavelength of the IR desorption laser. However, the observed wavelength dependence is counterintuitive; no desorption is observed at IR wavelengths resonant with strong IR active intra-molecular vibrational modes while strong desorption occurs only at wavelengths corresponding to absorption minima. The observed spectral structure can be consistently interpreted as resulting from the excitation of weak IR allowed combination modes, involving one quantum of an intra-molecular vibration and one quantum of an inter-molecular vibration. The accumulation of energy in the acoustical modes via this process during the macro-pulse eventually leads to desorption.

Electrical Transport and Phase Transitions in (AC60)_n

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The polymerized AC60 compounds (A=K, Rb, Cs) exhibit significantly differing electrical transport properties. KC60 is metallic from 350 K to 50 K, and becomes semiconductor-like below 50 K. The low-temperature transition can be suppressed by applied pressure.

The dc resistivity of RbC60 and CsC60, on the other hand, shows semiconducting behavior. We have found that applied pressure causes RbC60 to undergo an insulator-to-metal transition. The properties of this transition change significantly with additional applied pressure.

At no pressure or temperature does either KC60 or RbC60 exhibit any measurable magnetoresistance.

METAL-INSULATOR TRANSITION AND SUPERCONDUCTIVITY IN ALKALI-AMMONIA COMPLEX FULLERIDES

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We report synthesis of new alkali-ammonia-C60 superconductors, and electronic properties of ammoniated K3C60. We have synthesized new superconducting fullerides with the composition of (NH3)_xNaA2C60 (A=K, Rb, and x=0.5-1) from the solution of liquid ammonia. The compounds with one small Na cation and two large alkali cations, which has never been synthesized by conventional method, were successfully stabilized by incorporation of ammonia. All the observed x-ray diffraction peaks are indexed as fcc with the lattice parameter of 14.36Å and 14.52Å for K and Rb compounds, respectively. T_c's of these compounds are 14-11K and 18-10K for K and Rb compounds, dependent on ammonia concentration x. The volume fraction reached 60-100%, indicating the bulk nature of the superconductivity. These T_c's are significantly lower than the empirical rule. It is noteworthy that the cubic structure is maintained in the new monoammonia compounds in sharp contrast with NH3K3C60.

INVESTIGATIONS ON ISOMER AND MASS SELECTED CARBON CLUSTER IONS

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Investigations of the reactivity and the fragmentation processes of isomer and mass selected carbon cluster ions have been performed using a laser evaporation source in combination with both a linear and a reflectron time-of-flight mass spectrometer.

We can apply two different selection schemes to characterise the cluster ions: first isomer selection by chemical reaction during the generation process and secondly time-of-flight techniques for mass selection and analysis are possible. The reaction and fragmentation channels of the selected cluster ions can be determined by a subsequent collision cell with varying collision energies and reagents.

First results on the collision of mass selected fullerenes with various rare gases will be presented.

A SCANNING TUNNELING SPECTROSCOPY STUDY ON POLYCRYSTALLINE $\text{Rb}_2\text{CsC}_{60}$ AT 4.5 K

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The superconducting energy gap Δ of polycrystalline $\text{Rb}_2\text{CsC}_{60}$ ($T_c=32.8$ K) is determined at 4.5 K by tunneling spectroscopy using a low temperature scanning tunneling microscope. Most gap values range from 3.1 meV to 6.0 meV, with an average of $4.2 \text{ meV} \pm 0.7 \text{ meV}$ (extracted from a statistical sample of 45 spectra). We attribute the scattering to local variations of stoichiometry. However, some spectra exhibit much larger gaps ($\approx 7.9 \text{ meV}$). These large values cannot be understood within standard BCS-theory. We therefore suggest an alternative explanation by assuming a Superconductor-Insulator-Superconductor (SIS) tunnel junction. Such a contact can occur when a superconducting grain is picked up by the tunneling tip. In this case a gap width of 4Δ (peak to peak) is expected which is in agreement with our observed large values of $\approx 7.9 \text{ meV}$.

SUPERCONDUCTIVITY AND EPR AT EARLY STAGES OF DOPING PROCESS FOR K+C₆₀ SYSTEM

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Early stages of doping process of C₆₀ with potassium was investigated with the EPR and MMMA techniques. Before heating weak superconductivity of K+C₆₀ mechanically mixed system was found. Stronger diffusion of K ions into octahedral and tetrahedral sites of the fcc structure of C₆₀ during successive stages of doping process leads to well separated, below 100K, EPR narrow lines related to monovalent C₆₀¹⁻ anion ($g_1 \approx 2.0000$) and to the trianion C₆₀³⁻ ($g_3 \approx 2.0014$). Time dependent changes in the intensities of both C₆₀¹⁻ and C₆₀³⁻ lines were observed when the system undergoes an eutectoid transformation. New superconducting unstable phase with T_c (T_c⁽¹⁾=21K) higher then T_c for K₃C₆₀ concentration (T_c⁽²⁾=18.5) was found. The increase of external magnetic field distinctly separates these two superconducting phases. MMMA hysteresis confirm superconductivity in both temperature regions T<T_c⁽²⁾ and T_c⁽²⁾<T<T_c⁽¹⁾. New phase with T_c⁽¹⁾ appears in the early stages of doping when EPR C₆₀¹⁻ signal exist. When the doping process is brought to the end the EPR spectrum consist of a single EPR line of C₆₀³⁻ radical at $g_3=2.0013$ and the MMMA signal gives a single temperature T_c⁽²⁾=18.5K.

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SYNTHESIS AND CHARACTERIZATION OF THREE STABLE Tm@C₈₂ ISOMERS

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Endohedral thulium fullerenes have been produced and separated by a two stage HPLC method. Three stable Tm@C₈₂ isomers were detected and their purity was analyzed by mass spectrometry and HPLC. In the HPLC separation a strong shift of the retention times was observed in comparison to the behavior of other M@C₈₂ fullerenes (M=Sc, Y, La). The thulium isomers were characterized by UV-VIS-near-IR- and IR-spectroscopy and by cyclovoltammetry. They shown strong differences of the UV-VIS absorption. Their spectroscopic properties are also different from that of other known M@C₈₂ fullerenes (M=Y, La, Ce, Pr, Gd). The reasons for that differences are discussed with respect to the valence state of the thulium ion inside the cage.

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^{13}C NMR INVESTIGATIONS OF Cs_4C_{60}

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PTh 21 Three stable phases of Cs_xC_{60} are presently known in the phase diagram: Cs_1C_{60} , Cs_4C_{60} and the fully doped Cs_6C_{60} . Here we report on the semiconducting phase Cs_4C_{60} and compare the results with those of the other A_4C_{60} .

The relaxation rates T_1^{-1} and T_2^{-1} were measured as function of temperature. As in the case of Rb_4C_{60} and K_4C_{60} , electronic and reorientational contributions can be distinguished and are analyzed. It is found that the activation energy of the reorientational dynamics depends on the size of the counterion and increases with increasing radius of the alkali ion. However, the electronic activation energy is independent of the ion within the accuracy of the experiment.

In addition, variable temperature high resolution NMR techniques were applied in order to get some insight into the distribution of the electronic wavefunction. Since the reorientational activation energies are larger in the case of Cs_4C_{60} as compared to Rb_4C_{60} and K_4C_{60} , the activated electronic state is more pronounced and can be studied in more detail.

COMPLEXATION OF C_{60} WITH MULTISULFUR π -ELECTRON DONOR BET-TTF. SPECTROSCOPIC AND CRYSTAL STRUCTURE OF THE CHARGE-TRANSFER COMPLEXES $(\text{BET-TTF})(\text{C}_{60})(\text{SOLVENT})$.

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PTh 22 We report the synthesis and characterization of the ternary 1:1:1 charge transfer complexes formed by C_{60} , the π -electron donor *E*-bis(ethylenethio)-tetratetrafulvalene and solvent (toluene or chlorobenzene). Crystals of $\text{C}_{60}\cdot\text{BET-TTF}\cdot\text{C}_7\text{H}_8$ and $\text{C}_{60}\cdot\text{BET-TTF}\cdot\text{C}_7\text{H}_5\text{Cl}$ are isostructural. X-ray analysis reveals that its structure consists on planes of C_{60} separated by chains of BET-TTF and disordered solvent. Distances between fullerene centers along b and c directions are short (10.023 Å), promoting close contacts between molecules inside the plane, in spite of these contacts, the crystals are electrical insulators. This result is accounted for the very low degree of charge-transfer between donor and acceptor molecules revealed in their electronic and EPR spectra.

Keywords : charge-transfer, TTF, x-ray, EPR

SPIN-DEPENDENT PHOTOCONDUCTIVITY OF A C₆₀ / OLIGOTHIOPHENE HETEROJUNCTION

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PTh
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Recombination and transport of photoinduced charge carriers can be affected by their spin state or by the spin state of paramagnetic defects. This phenomenon is known as spin-dependent photoconductivity. We report on investigations of thin polycrystalline films (about 100 nm thickness) of C₆₀ and various oligo-thiophenes, as well as compounds of these materials. Non-linear I/V-characteristics are observed. Changes of the photoconductivity on the order of 10⁻² under resonance conditions allow the observation of ESR signals with high signal to noise ratio, whereas direct ESR detection is impossible because of sensitivity reasons. The signal analysis with respect to microwave power, photocurrent, modulation frequency and temperature yields contributions of the individual layers and of the interface between different layers.

ANGLE-RESOLVED PHOTOEMISSION STUDY OF THE K COVERED C₆₀ MONOLAYER ON Au(110)

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PTh
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The electronic structure of the perfectly ordered C₆₀ monolayer adsorbed on Au(110) and intercalated with K has been studied using angle-resolved photoemission spectroscopy with 13eV synchrotron radiation photons at low temperatures. The K content was chosen appropriately to achieve a charge transfer very close to 3 electrons/C₆₀ molecule. It is shown that the sharp *t*_{1u}-derived peak located at 0.09eV below *E*_F in normal emission disperses towards the HOMO while going from $\bar{\Gamma}$ to \bar{M} with respect to the overlayer's surface Brillouin zone. This supports predictions given by LDA band structure calculations of a hexagonal closed-packed C₆₀ overlayer on Cu(111)(1×1)¹. Additional vibrational satellites exist at around 0.25eV and 0.5eV binding energy. The bandwidth of the entire spectral profile is 0.8eV what is considerably smaller than that of the *t*_{1u}-derived features in the bulk compound K₃C₆₀.

EXAFS STUDY OF LOCAL STRUCTURE AND SITE PREFERENCE IN SUPERCONDUCTING A_2BC_{60} SYSTEMS ($A = K, Rb$; $B = Rb, Cs$)

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PT_h
25

X-ray absorption spectroscopy (EXAFS) at the alkali ions K, Rb and Cs was applied to study site preference and local structure in ternary A_2BC_{60} systems (K_2RbC_{60} , K_2CsC_{60} , Rb_2CsC_{60}). Similar to a previous study of $K_{3-x}Rb_xC_{60}$ [1] we found a strong site preference of the smaller alkali ions (A) for the tetrahedral sites and of the larger ions (B) for the octahedral sites. Such a preferential site occupation is actually observed in all present systems. From temperature dependent EXAFS measurements (20 K - 300 K) we derived the temperature dependence of the A-C distance, which gives direct information about the thermal expansion and, from the Debye-Waller factor, about the local binding strength. The EXAFS data for the B ions, Rb in K_2RbC_{60} and Cs in K_2CsC_{60}/Rb_2CsC_{60} , give clear evidence for an off-center position of the B ions at the octahedral sites. The present EXAFS data are discussed in conjunction with XRD, NMR and susceptibility measurements performed on the same samples.

VIBRATIONAL STRUCTURE OF $Sc_2@C_{84}$ ANALYSED BY IR SPECTROSCOPY

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The isomer III of $Sc_2@C_{84}$ was separated by multi-cycle HPLC purification and subsequently condensed on a small area of a gold substrate. The condensed compound was baked for 8 hours at 450 K in high vacuum to get rid of enclosed solvents, prior to any experimental investigation.

We present temperature dependent IR absorption measurements of $Sc_2@C_{84}$ which have been performed between 50 and 300 K and between 400 and 5000 cm^{-1} , respectively. The vibrational structure of the endohedral compound is compared to the structure of unfilled C_{84} . We find a strong overall broadening of the vibrational modes in $Sc_2@C_{84}$. Also some of the vibrational absorption lines are strongly enhanced if compared to the spectrum for the empty cage. With decreasing temperature a dramatic narrowing of the lines in the spectral range between 700 and 800 cm^{-1} is observed. A charged phonon effect and a coupling of the diffuse or vibrational motions of the Sc_2 molecule in the cage are considered as a possible explanation for the observed results.

ESR studies on $\text{Na}_2\text{Cs}_x\text{C}_{60}$ ($0 < x < 1$)

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In this communication, we report the density of states on four $\text{Na}_2\text{Cs}_x\text{C}_{60}$ single phase solid solution compounds, with $0 \leq x \leq 1$. Those compounds all show $\text{Pa}\bar{3}$ structure order below 300 K and the first aim of their synthesis was to study the effect of C_{60} molecular valence on T_c . When $0.5 < x \leq 1$, they are superconductors with T_c equal to 11.5 K and 7 K for respectively $\text{Na}_2\text{Cs}_1\text{C}_{60}$ and $\text{Na}_2\text{Cs}_{0.75}\text{C}_{60}$. When $x \leq 0.5$, no superconductivity has been detected down to 2 K so far. Our ESR susceptibility measurement allow us to conclude that they are nonetheless metallic, except Na_2C_{60} , which remains insulating at all temperature. We will discuss the interplay between the singlet-triplet equilibrium susceptibility that we evidenced in Na_2C_{60} and the Pauli susceptibility in $\text{Na}_2\text{Cs}_x\text{C}_{60}$.

Some new aspects for doping of higher fullerenes

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Recent calculations on C_{80} [1] predict the isomers with D_2 and D_5 symmetry to be energetically most favorable and most stable. Using photoemission (XPS, UPS) and C1s near-edge x-ray absorption fine structure (NEXAFS), we studied the occupied and unoccupied electronic structure of this fullerene that has only recently become available. Since a peak signal strength in UPS cannot directly be identified with the degeneracy of the corresponding electronic level, a comparison with theory to identify actually prevailing isomers is not straightforward. NEXAFS on doped $\text{Rb}_{4.5}\text{C}_{80}$, however, allowed us to deduce degeneracies of the lowest unoccupied bands and thus to show rigorously that the D_5 isomer alone cannot explain the UPS spectra of undoped and doped C_{80} . An admixture of the D_2 isomer is consistent with our data.

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Transmission NEXAFS from air-exposed $\text{La}@\text{C}_{82}$ exhibits a strong shoulder below the C1s edge, similar to the one we observe for the undoped parent material C_{82} . Heating the $\text{La}@\text{C}_{82}$ films up to 700 °C reduces the intensity of this shoulder substantially; subsequent exposure to pure oxygen restores it in part. This behavior may indicate a doping effect of oxygen in $\text{La}@\text{C}_{82}$: electrons donated by La to the C_{82} cage are partially removed by oxygen.

[1] K. Kobayashi, S. Nagase, and T. Akasaka, Chem. Phys. Lett. **245**, 230 (1995).

B₃₂ AND C₆₀⁶⁻: TWO CASES OF LOST ICOSAHEDRAL SYMMETRY

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PTTh
29 The duality relationship transforms any standard fullerene in a polyhedron with triangular faces only. Then, B₃₂ comes as a topological analogy of C₆₀. The topological symmetry of B₃₂ is again I_h. The icosahedral species, however, is not a local energy minimum at the HF/STO-3G and HF/3-21G *ab initio* level. We have found imaginary vibrational frequencies in both HF/STO-3G and HF/3-21G treatments (though not related to a Jahn-Teller distortion). Hence we deal with higher saddle points - the symmetry must be relaxed, this being followed at a semiempirical level. In the MNDO computations the cage relaxes into a D_{2d} symmetry. Atomization heat is used in evaluation of its stability. Similar event can be observed with C₆₀⁶⁻. The hexaanion is not subjected to Jahn-Teller distortions, however, computations at the MNDO, AM1, PM3, SAM1, HF/STO-3G and HF/3-21G levels show that relaxed, non-icosahedral cage of C₆₀⁶⁻ is lower in energy. The computed energy gain varies between 60 and 150 kJ/mol and thus, it is consistently significant.

On a leave from the Academy of Sciences of the Czech Republic, Prague.

SOLUTION SYNTHESIS AND CHARACTERIZATION OF SINGLE PHASE METALLIC Cs₃C₆₀

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2) Japan Advanced Institute of Science and Technology

3) AT&T Bell Laboratories, U.S.A.

PTTh
30 We previously reported that Cs₃C₆₀ can be synthesized through the liquid ammonia route at low temperature, and observed superconductivity at 40K when the sample was pressurized [1]. Although all the C₆₀ molecules were found to be in the 3- valence states as expected for Cs₃C₆₀, x-ray diffraction indicated that it has both cubic A15 and body-centered tetragonal (bct) phases.

By controlling the experimental conditions, we have succeeded in obtaining a Cs₃C₆₀ compound with the bct structure only. The compound has been characterized by powder x-ray diffraction, Raman spectroscopy, DC magnetization and electron spin resonance measurements. The frequency of the C₆₀ A_g mode is down-shifted from 1468.8 cm⁻¹ to 1448.8 cm⁻¹ after doping, indicating 3- valence. ESR and DC magnetization measurements reveal that the compound is conducting at room temperature.

A COMPARATIVE NMR INVESTIGATION OF THE LOW TEMPERATURE PHASES OF AC_{60}

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PTh
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Whereas all AC_{60} compounds are found in a fcc rock salt structure at temperatures above 400-450K, a variety of stable and metastable low temperature phases exists, depending on the thermal treatment of the sample. We present NMR data on the low temperature polymer phase and on the transition into the magnetically ordered phase below 50 K for different AC_{60} ($A=K,Rb,Cs$). Static and high resolution ^{13}C spectra show a close analogy between the polymer phase of RbC_{60} and CsC_{60} . The magnetic phase transition is monitored by an increase of the second moment as well as an increase of the spin lattice relaxation rates of the ^{13}C and alkali nuclei. Here again, RbC_{60} and CsC_{60} show a very similar behaviour. The results are compared with ^{13}C NMR data of the quenched metastable phase of KC_{60} .

MAGNETIC PROPERTIES OF $TDAE-C_{60}$

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Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan

K. TANAKA, T. SATO and T. YAMABE

Kyoto University, Division of Molecular Engineering, Kyoto, Japan

Magnetic properties of a molecular soft ferromagnet $TDAE-C_{60}$ ($TDAE$; PTh
tetrakis(dimethylamino)ethylene) are studied. Precise measurements of low-field magnetization of
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 $TDAE-C_{60}$ by SQUID magnetometer revealed a clear "remanence" or "irreversibility", i.e. difference in the temperature dependence of magnetization between zero-field cooled (ZFC) and field cooled (FC) conditions below the freezing temperature T_f around 10 K.¹⁾ This result is consistent with our previous observation of a cusp in the temperature dependence of nonlinear ac susceptibility around 10 K.²⁾ In addition, an extremely slow relaxation phenomena of magnetization and the stretched exponential type time-dependence, characteristic of a spin-glass-like freezing process, was observed at low temperatures.¹⁾ We found that ZFC magnetization (M_{ZFC}) was always drifting upwards, so that the actual temperature dependence of M_{ZFC} is irreversible and depends on the warming speed and measurement time.

These "glassy" characteristics are reminiscent of a "spin-glass" with T_f at about 10 K as the nature of the magnetic ground state of $TDAE-C_{60}$, although the temperature dependence of magnetic moment at higher temperature behaves rather like a ferromagnet with a transition temperature $T_C \sim 16$ K.

Polymeric Fullerenes

- 8:30 – 9:00 G.E. SCUSERIA, Rice University, Houston, USA
Theoretical Studies of Polymerized Fullerene Structures
- 9:00 – 9:30 A. SOLDATOV, Umea University, S
Pressure Polymerized C₆₀: Raman and NMR Studies
- 9:30 – 10:00 T. FRAUENHEIM, Technische Universität, Chemnitz, FRG
Structure, Stability and Vibrational Properties of Polymerized C₆₀
- 10:00 – 10:30 Coffee break
- 10:30 – 11:00 B. BURGER, Universität Wien, A
Dimer and Cluster Formation in C₆₀ Photoreactions
- 11:00 – 11:30 R. EDER, University of Groningen, NL
Excitonic Dispersion and Nonlinear Optical Response of Excitons in Solid C₆₀
- 11:30 – 12:00 M. MUCCINI, Istituto di Spettroscopia Molecolare, Bologna, I
Frenkel and Charge-transfer Excitons in Solid C₆₀
- 12:00 – 17:00 Mini Workshops

Photonics of Fullerenes

- 17:00 – 17:30 Z.V. VARDENY, University of Utah, Salt Lake City, USA
Excited States Spectroscopy of C₆₀ and C₇₀: Isolated Molecules and Thin Films
- 17:30 – 18:00 R. JACQUEMIN, Institut für Festkörperforschung, Jülich, FRG
F-Sec Time-Resolved Two-Photon Photoemission of C₆₀ Films
- 18:00 – 18:30 H. RIETSCHEL, Forschungszentrum Karlsruhe, FRG
— SUMMARY —

Farewell Dinner

THEORETICAL STUDIES OF POLYMERIZED FULLERENE STRUCTURES

Gustavo E. Scuseria

Center for Nanoscale Science And Technology,
Rice Quantum Institute and Chemistry Department MS-60,
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8:30
POFU
1

Solid fullerite has at normal pressure and temperature an FCC structure of weakly interacting freely rotating polyhedra. As the temperature is lowered, Coulomb interactions lock the spheres into an orientationally ordered simple cubic (SC) phase. Heating under high-pressure drives C₆₀ to new distorted crystalline phases that are metastable at room temperature and pressure. Three different distortions have been experimentally characterized. Theoretical calculations in our research group employing the tight-binding method support the view that these new carbon phases can be understood as the long range order polymerization of C₆₀ through cycloaddition reactions that are at the origin of the shorter intermolecular distances. In this paper, we also report the results of calculations using *ab initio* Hartree-Fock and density functional methods on these cycloaddition reactions between C₆₀ molecules.

PRESSURE POLYMERIZED C₆₀: RAMAN, IR AND NMR STUDIES.

P. Jacobsson, P-A. Persson, A. Soldatov and B. Sundqvist
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and

J. Edlund and D. Johnels
Department of Organic Chemistry, Umeå University, S-901 87, Umeå, Sweden

9:00
POFU
2

ABSTRACT

The properties of bulk C₆₀ have been studied after treatment at 1.1 GPa and 550-585 K. The treated material is insoluble in both toluene and 1,2-dichlorobenzene. Raman and IR studies on modified material show a large number of new lines, and the Raman pentagon pinch mode shifts from 1469 to 1458 cm⁻¹ as on photopolymerization. MAS NMR shows one broadened line at the original C₆₀ shift 144 ppm and a small peak at about 77 ppm due to the bridging carbons. The results verify previously suggested polymeric structures where the fullerene cages are connected by four-membered rings. We discuss in detail a reverse transformation to normal C₆₀ on heating.

Structure, Stability and Vibrational Properties of Polymerized C₆₀

Dirk Porezag, Th. Frauenheim and Th. Köhler

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Mark R. Pederson

Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C.
20375

9:30
POFU
3

We have applied a density-functional based nonorthogonal tight-binding (DF-TB) method to study the structure, energetics and vibrational properties of five different [C₆₀]_N-oligomers (N=2, 3, and 4). Although most of the work was devoted to neutral clusters, we have also determined the vibrational spectrum of a [C₆₀]₂²⁻ structure. These charged clusters may be a more realistic model for Alkali metal atom intercalated Fullerene solids. In order to compare our results with the experimental spectra, Raman intensities have been calculated for each cluster using the bond polarization model. To address the energetics associated with polymer stability, we have calculated the DF-TB reaction barrier for the dissociation of the C₆₀ dimer along two different paths. The cohesive energy and the Raman-active interball mode of the C₆₀ dimer have been investigated with an all-electron, self-consistent Density-functional based method also. We compare our results with recent experimental data.

Dimer and Cluster Formation in C₆₀ Photoreaction

B. Burger, J. Winter and H. Kuzmany, Universität Wien, Institut für Festkörperphysik
Strudlhofg. 4, A-1090 Wien, Austria.

10:30
POFU
4

The process of phototransformation was analyzed by means of Raman spectroscopy for single crystals and thin film samples at various temperatures. Characteristic features in the resulting spectra were found to depend on the illumination temperature. A comparison with calculations of Porezag et al. was performed, from which the material irradiated at high temperatures was assigned to a C₆₀ dimer. The material illuminated at room temperature could not be identified with a simple cluster.

Exciton Dispersion and Nonlinear Optical Response of Excitons in Solid C_{60}

R. Eder, A.-M. Janner, and G. A. Sawatzky

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University of Groningen, 9747 AG Groningen, The Netherlands

Non linear optics experiments in solid C_{60} have revealed the existence of a number of excitonic states at energies well below the optical gap. Motivated by these results we have performed a theoretical study of the dispersion of Frenkel-type excitons in the low-temperature $Pa3$ phase of solid C_{60} . Exciton propagation is accomplished by an exchange-like two-step process, where an electron-hole pair on a given C_{60} molecule is split by the inter-molecular kinetic energy and recombines on a neighboring molecule. We apply our results to the theoretical calculation of the nonlinear optical susceptibility for second harmonic generation (SHG) for which we find reasonable agreement with experiment. Our results suggest near-degeneracy of the molecular T_{1g} and G_g multiplet, and a relatively low charge transfer energy between nearest neighbors.

11:00
PHOT
1Frenkel and charge-transfer excitons in solid C_{60}

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Solid C_{60} shows the typical characteristics of a molecular solid in which the molecules are weakly held together by Van der Waals forces. "On ball" electronic excitations in the solid are therefore very close in energy and nature to those of the free molecule. The lowest electronic excitations in solid C_{60} are tight bound (Frenkel) excitons. Clear evidence of this is given by absorption, one and two-photon excitation, and photoluminescence spectroscopy. Further to this neutral excitations which are bound to the individual molecule there are charged excitations corresponding to the promotion of electrons from ball to ball and from ball to the free electron continuum. We observe intermolecular charge-transfer excitons (CTE) by measuring the electroabsorption (EA) of thin films at liquid helium temperature. The analysis of the EA spectrum in terms of linear and quadratic Stark effect allows the identification of two low-energy charge-transfer excitons at 2.45eV and 2.82eV.

These findings set the singlet exciton binding energy $E_{ex} \geq 0.5eV$.

11:30
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2

EXCITED STATES SPECTROSCOPY OF C_{60} AND C_{70} : ISOLATED MOLECULES AND THIN FILMS. Zeev V. Vardeny, X. Wei, D. Dick. University of Utah, Salt Lake City, UT.

An overview of optical data from isolated molecules and thin films of C_{60} and C_{70} using a wide variety of techniques will be presented to develop a model of the excited-energy states of these materials and their dynamics. The techniques employed include cw and ps transient absorption, photoluminescence, resonant Raman scattering, absorption-detected magnetic resonance (ADMR), and electroabsorption spectroscopy.

17:00
PHOT

3

The thin film absorption spectra have broader bands which are red-shifted from the solution data. In addition, transitions near 2.3 eV which are forbidden in isolated C_{60} molecules become weakly observed in the absorption spectra of thin films and appear to have a strong effect on the resonance Raman scattering profiles. Photoluminescence-excitation and integrated-electroabsorption spectra also peak near 2.3 eV. Similar results are observed for C_{70} thin films with a small (~ 0.1 eV) red shift from 2.3 eV.

When excited below the energy gap near 2.3 eV, the primary photoexcitations in C_{60} are localized singlet excitons. A small fraction of the singlet excitons decay into the triplet manifold at $t > 3$ ns forming long-lived triplet excitons and charged polarons with characteristic spin 1 and $1/2$ ADMR signals, respectively.

F-SEC TIME-RESOLVED TWO-PHOTON PHOTOEMISSION OF C_{60} FILMS

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We have developed the experimental technique of two-photon photoemission (2PPE) to investigate the time-dependent scattering processes in electronically excited semiconductors. Here we report first results on C_{60} films deposited onto an Au substrate showing the dynamics of excited electrons in the two lowest conduction bands.

17:30
PHOT

4

In a first step, a photon of appropriate energy is absorbed by an electron which is excited into an unoccupied state. Due to this effect, the first photon is called "pump" photon. A second photon ("probe") which is delayed by a well-defined time interval is used to photoemit this excited electron subsequently. Hence, the probe photon maps the occupation of the conduction band states. By variation of the time delay between both photons, the lifetime of the excited state can be measured directly. The lifetimes have then to be interpreted in terms of scattering processes and relaxation mechanisms.

If both photons arrive at the sample simultaneously, the "native" excitation is generated. In this case, we observe structures at 2.2 and 3.0 eV measured relative to the emission of the HOMO in the photoemission spectrum. The peak at 3.0 eV vanishes within a picosecond, whereas the intensity of the other structure increases for approximately 10 ps. After this time, a third structure at 1.8 eV develops in the spectra becoming dominant within the next 200 ps.

We interpret the fast relaxing peak at 3.0 eV above the energy of the HOMO as due to the electrons excited by the direct optical transition from the valence band into the second lowest conduction band of C_{60} . The structure at 2.2 eV corresponds to free electrons in the lowest conduction band (LUMO). Due to the dynamic evolution of the system, those electrons can be trapped by holes such that singlet excitons of C_{60} with an energy of 1.8 eV result. This interpretation is consistent with the decrease of the intensity of the peak at 2.2 eV and the simultaneous increase of the photoemission intensity at 1.8 eV.

18:00
SUMM

CONTRIBUTORS

Abe S.	Tu17	Ceppek C.	AXC606	93
Adamchuk V.K.	Th11	Cermak I.	FNST2	
Adamowicz L.	Th29	Cevc P.	Th6, C60-2	
Adelmann P.	Th10, Th28	Chauvet O.	CNTB6	
Ajayan P.M.	Sp3	Chen Y.K.	CNTB2	
Akasaka T.	Sp1	Churilov G.N.	Th7	
Alloul H.	Sp4, AC604	Copley J.R.D.	Tu25	
Almeida Murphy T.	Tu1	Cummins T.R.	Th28	
Andersson S.	AXC605, NFST1	Curioni A.	Sp5, HETF2	
Andreoni W.	Sp5, HETF2	Curran S.	Th8	
Angyan J.G.	Sp19	Da Ros T.	CHEM3	
Arcon D.	Th1, Th6, C60-2	Dashkova E.V.	Tu5	
Armbruster J.F.	Th28	Davey A.P.	Th8	
Arvanitis D.	Tu7, NFST1	Degiorgi L.	CNTB5	
Averdung J.	CHEM2	Delfs H.	Tu8	
Bacsa W.	Th3, CNTB5, CNTB6	Dementjev A.	Tu9	
Bagramov R.H.	APPL2	Denninger G.	Sp2	
Ballenweg S.	Th12	Dick D.	PHOT3	
Balooch M.	APPL4	Ding A.	Tu8, Th17	
Banhart F.	Tu2	Dinse K.-P.	Th5, ENDO2	
Bartl A.	Th2, CHEM4	Dolinar P.	Tu10	
Baumann R.	Tu3	Dolinsek J.	Th1	
Baumgartner G.	CNTB6, Th3	Drechsler S.-L.	Tu13	
Becker R.	Tu20	Dubitsky G.A.	APPL2	
Belkir H.	Tu22	Dumas P.	Sp17	
Belz T.	Tu4, Tu6, Th13	Dumschat J.	Sp21	
Bendele G.	Th4, AC603	Dunsch L.	Tu21, Th2, Th20,	
Benito A.M.	CNTB3		Sp6	
Bennati	Sp2	Eberhardt W.	PHOT4	
Bensch W.	Sp21	Eder R.	PHOT1	
Benz M.	Sp16	Ederle Y.	Tu23	
Bernier P.	Sp3	Edlund U.	POFU2	
Bianco A.	CHEM3	Eickelkamp T.	Th9	
Biro L.P.	Sp19	Eisler H.	ENDO1	
Blank V.D.	APPL2	Eletskii A.V.	Tu11	
Blau W.	Th8	Elisabelle E.	Tu22	
Blinic R.	Th1, Th6, C60-2	Faigel G.	Sp12, AC603	
Boltalina O.V.	Tu5	Faiman D.	Tu16	
Boman M.	APPL1	Fanti M.	ENDO1	
Bommeli F.	CNTB5	Feldman Y.	NFST3	
Bortel G.	Sp12, AC603	Feldman Y.	Tu12, ENDO2	
Braun Th.	Tu6	Fink J.	Th26, Sp16	
Brezova V.	Th5	Fischer A.	Th10	
Brink v.d.J.	AXC604	Fischer J.E.	Th4, Th27, AXC601,	
Brouet V.	Sp4, AC604		AXC602, AXC603	
Bruhwiller P.A.	Tu7, AC601, NFST1	Forro L.	Th3, Sp4, Sp7, Sp9,	
Buga S.G.	APPL2		Sp12, AC601, AC602, AC603,	
Burger B.	POFU4	Frauenheim T.	AC604, AC606, CNTB5,	
Bürk M.	Th28, Sp16	Frey G.L.	CNTB6	
Byrne H.J.	Tu17	Fuchs D.	POFU3	
Byszewski P.	Tu18	Füller T.	Tu12, NFST3	
Campbell E.E.B.	ENDO3	Fünffinger M.	Th10, Th28, ENDO1	
Carrard M.	Th3, AC601, CNTB6	Gasiorowski R.	Tu2	
Caudano R.	Tu22, Sp17	Ghijsen J.	Sp15	
		Goldoni A.	Tu21	
			Tu22	
			AXC606	

94	Gompf F.	AC607	Kern K.	Tu20
	Goren S.	Tu16	Khazeni K.	Th15
	Gorovikov S.A.	Th11	Kim M.S.	Tu30
	Gotschy B.	Sp18	Kino N.	Tu30
	Goze C.	Th21, AC605	Kirbach U.	Th2, Th20, CHEM4
	Granasy L.	Sp12, AC603, AC606	Kisio K.	Tu30
	Gray S.M.	NFST1	Kitazawa K.	Tu30, Sp13
	Green M.L.H.	CNTB2	Kleinbub O.	Th21
	Gromov A.	Th12	Knauff O.	Sp16
	Grupp A.	Th23, Sp2, Sp6	Knorr S.	Sp6
	Grushko Y.	Th13, Sp21	Knuper M.	Sp16
	Gunnarsson O.	C60-1	Köhler T.	POFU3
	Güntherodt H.-J.	Th18	Koinuma H.	Tu30
	Gutierrez R.	Tu13	Kolesnik S.N.	Sp21
	Hamza A.	APPL4	Koller D.	Sp9
	Hare J.P.	CNTB3	Koretz A.Y.	Th7
	Hassanien A.	APPL3	Krämer H.	Tu3
	Hasselstrom J.	Tu7	Krätschmer W.	Th12, FNST2
	Havlik D.	Tu14	Kraus S.	PHOT4
	Heer de W. A.	Th3, CNTB4, CNTB6	Krawez N.	ENDO3
	Heid R.	AC607	Kroto H.W.	CNTB3
	Helden von G.	Th14	Krüger U.	Sp2
	Henke S.	Sp15	Krumeich F.	Tu3
	Hennrich F.	ENDO1	Kucharski Z.	Tu18
	Herein D.	Sp21	Kuhnke K.	Tu20
	Hernnäs B.	NFST1	Kuroshima S.	NFST5
	Hertel I.V.	ENDO3	Kürti J.	Tu19
	Hevesi K.	Sp17	Kutner W.	Tu21
	Hirsch A.	Tu27, CHEM1	Kuzmany H.	Tu14, Tu15, TH26
	Hodeau J.-L.	Sp8		POFU4, Sp20
	Höhne M.	Tu1	Lafontaine E.	AC604
	Holleman I.	Th14	Lang H.P.	Th18
	Homyonfer M.	Tu12, NFST3	Langlais V.	Tu22
	Hone J.	Th15	Lätsch S.	Tu3
	Hsu W.K.	CNTB3	Lazar A.	Sp19
	Huang Ch.	Tu22	Lazzeri P.	Sp10
	Hubler U.	Th18	Lebedkin S.	Th12
	Hulman M.	Tu14, Tu15	Lee S.-L.	Tu28, Th29
	Hunt M.R.C.	AXC606	Lefrant S.	Sp3
	Iwasa Y.	Th16, Th30	Lehner C.	ENDO1
	Jacobsson P.	POFU2	Li L.	Tu30
	Jacquemin R.	PHOT4	Liangbing G.	Tu22
	Janner A.-M.	PHOT1	Llacay J.	Th22
	Jantoljak H.	Th17	Lorents D.C.	Sp10
	Jess P.	Th18	Los S.	Th19
	Jiang L.Q.	Sp10	Lu D.H.	Th28
	Johansson L.S.O.	NFST1	Lucas A.A.	FNST1
	Johansson M. K.-J.	NFST1	Lüders K.	Th18
	Johnels D.	POFU2	Luftmann H.	CHEM2
	Kallay M.	Tu26	Lui A.	Sp10
	Kamaras K.	Sp7	Maggini M.	CHEM3
	Kappes M.M.	Th10, Th28, Sp16,	Maier A.	Th23
		ENDO1	Malhotra R.	Sp10
	Karis O.	NFST1	Malier L.	AC604
	Katz E.A.	Tu16	Mancini C.	NFST1
	Kazaoui S.	Tu17	Manini N.	C60-1
	Kempinski W.	Th19	Maniwa Y.	Th16

Manteca-Diego C.	CNTB3	Porezag D.	POFU3
Manzke R.	Th24	Prassides K.	CNTB3, HETF3
Marques L.	Sp8	Prato M.	CHEM3
Martensson N.	Tu7, NFST1, AXC605	Prudnikova G.V.	Th11
Martin M.C.	Sp9	Putter M.	Th14
Martin T.P.	NFST4	Rachdi F.	Th21, Th31, AC605, AXC603
Mas M.	Th22		Th5
Maser W.K.	Sp3	Rapta P.	Sp15
Mathis C.	Tu23	Rauschenbach B.	CNTB3
Mattay J.	CHEM2	Reid D.G.	AC607
Maxwell A.J.	Tu7, NFST1, AXC605	Renker B.	ENDO1
Mehring M.	Th21, Th 23, Th31, Sp2, Sp6, AC605, AXC603	Richard S.	Th10
	Tu24, Th14	Rietschel H.	Th27, AXC602
Meijer G.	Tu24	Robert J.	Th8, Th9
Meingast C.	Tu25	Roth S.	Th22
Michel K.H.	Th10, Th28, Sp16, ENDO1	Rovira C.	ENDO2
Michel R.H.	Th1, Th6, APPL3, C60-2	Rübsam M.	Tu22, Th24, Sp17, AXC605
Mihailovic D.	Sp9, AC601	Rudolf P.	Th13
Mihaly L.	Tu17		Sp10
Minami N.	Th16	Ruehle T.	FNST3
Mitani T.	Th16	Ruoff R.S.	FNST3
Miyamoto Y.	AXC606	Saito Y.	Tah24
Modesti S.	Sp3	Sakata	Th32
Molinie P.	Th22	Saltas V.	AXC604, PHOT1
Molins E.	FNST2	Sato T.	Th19
Monninger G.	Sp10	Sawatzky G.	Tu27
Moro L.	Th6, APPL3	Scharff P.	Sp18
Mrzel A.	PHOT2	Schick G.	CHEM2
Muccini M.	Th24	Schilder A.	Tu4, Tu6, Th13, Th18, Th25, Sp21
Müller A.	APPL3	Schlachter I.	Th28
Musevic I.	FNST4	Schlögl R.	AC607
Nagase S.	Tu24		Tu10, Tu14
Nagel P.	Tu19, Tu26, Sp19	Schmidt M.	Sp18
Nemeth K.	Sp11	Schober H.	Th28
Nguyen Manh T.	CHEM3	Schranz W.	ENDO2
Novello F.	Th25, Sp21	Schuetz W.	CHEM3
Nowitzke G.	Th28	Schuppler S.	POFU1
Nücker N.	Sp8	Schweitzer P.	Th2
Nunez-Regueiro M.	Th1, Th6, APPL3, C60-2	Scorrano G.	Tu16
Omerzu A.	Tu28	Scuseria G.E.	Th11
Osawa E.	CNTB3	Seifert G.	Th16
Osman O.I.	Sp12, AC603	Shames A.	Th26, FNST3
Oszlanyi G.	Tu30, Sp13	Shikin A.M.	Tu16
Ozawa M.	Th30	Shimoda H.	Tu5
Palstra T.T.M.	Sp14	Shinohara H.N.	CHEM2
Passerone D.	Sp10	Shtutina S.	Sp11
Paul A.	Tu1	Sidorov L.N.	APPL1
Pawlik Th.	POFU3	Siedschlag Ch.	Tu28, Th29
Pederson M.R.	Sp7, AC603, AC606	Sitter H.	Th13
Pekker S.	POFU2	Sjöström H.	POFU2
Persson P.-A.	Th27, AXC602	Slanina Z.	Th32
Petit P.	Sp15	Smirnov B.	Tu1
Philipp M.	Th26, Sp16	Soldatov A.	APPL1
Pichler T.	Tu21	Song Y.S.	Th19
Pietraszkiewicz M.	Tu1	Spaeth J.-M.	
Pietzak B.	Th1	Stafström S.	
Pokhodnia K.		Stankowski J.	

Stasko A.	Th5	Yamabe T.	Th32
Stephens P. W.	Th4, Sp12, AC603	Yamamoto E.	Th26
Stifter D.	Sp11	Yamanaka K.	Tu30
Stopka-Ebeler	FNST2	Yildirim T.	Th27, AXC602
Stritzker B.	Sp15	Yoshida M.	Tu28
Sundgren J.-E.	APPL1	Yoshinari Y.	Sp4, AC604
Sundqvist B.	POFU2	Yu L.-M.	Tu22
Surjan P.R.	Tu26, Sp19	Zamboni R.	PHOT2
Suwalski J.	Tu18	Zerbetto F.	ENDO1, NFST2
Takata M.	FNST3	Zettl A.	Th15, CNTB1
Taliani C.	PHOT2	Zhou O.	Th30, NFST5
Tanaka K.	Th32	Zimmer G.	AXC603, AC605
Tanigaki K.	NFST5	Zuppiroli L.	Th3
Tanigaki K.	Th30	Zwanger M.	Tu2
Tanner D.B.	Sp7		
Tarres J.	Th22		
Tegze M.	AC606		
Tellgmann R.	ENDO3		
Tenne R.	Tu12, NFST3		
Terrones H.	CNTB3		
Terrones M.	CNTB3		
Themlin J.-M.	Tu22		
Thier K.-F.	Th21, Th31, AC605		
Titarenko Y.N.	Th7		
Tjeng H.	AXC604		
Tokumoto M.	Th32		
Toniolo C.	CHEM3		
Torres-Garcia G.	CHEM2		
Tosatti E.	Sp14, C60-1		
Trybula Z.	Th19		
Tsang S.C.E.	CNTB2		
Uchida Y.	Th13		
Udvardi L.	Tu29		
Uhlik F.	Th29		
Vanzetti L.	Sp10		
Vardeny Z.V.	PHOT3		
Veciana J.	Th22		
Venturini P.	Th1		
Verheijen M.A.	Tu24		
Voekel G.	Sp18		
Vorobev V.S.	Tu11		
Vries De M.S.	Tu3		
Wachter P.	CNTB5		
Walton D.R.M.	CNTB3		
Weckwerth R.	Th17		
Wei X.	PHOT3		
Weidinger A.	Tu1		
Weis P.	Th10		
Werner E.	ENDO1		
Werner H.	Th18, Th25, Sp21		
Williams G.P.	Sp17		
Winter J.	Sp20, POFU4		
Wochner P.	Sp9		
Wohlens M.	Tu6		
Wolf Ch.	Tu1		
Wortmann G.	Th25, Sp21		
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